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Vol. 37 No. 327 March 1951

A SYMPOSIUM ON SPECTROSCOPIC METHODS IN THE PETROLEUM INDUSTRY

An ordinary general meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, December 6, 1950, Professor F. Morton, Vice-President, in the chair.

The Minutes of the preceding Ordinary General Meeting, held on November 8, 1950, were read, confirmed, and signed.

The General Secretary (D. A. Hough) announced the names of members elected since the last meeting of the Institute.

Professor F. Morton said: It is, I think, six years ago that we last had a discussion in this Institute on spectroscopic methods; on that occasion Dr Thompson and Dr Sutherland outlined their programmes for forward research in spectroscopy, at the time when the Institute was undertaking to begin the necessary financing of this job of work. We are very pleased to have Dr Thompson with us this evening, so that we may preserve the continuity of the study; and we regret that we have not the pleasure of Dr Sutherland's presence, for he is in the United States.

The Spectroscopic Panel is, strictly speaking, our senior panel, for the Hydrocarbon Research Group was financed to promote research in spectroscopy in connexion with hydrocarbons. Mr F. Gill, of the Anglo-Iranian Company, is the Chairman of the Spectroscopic Panel, an office which he has held since Professor Le Févre went to Australia in 1946 or early 1947. I invite him to introduce the subject matter which it is proposed to discuss.

Mr F. Gill: I would like to explain to you why we have arranged this symposium in the way we have and why we have tried to put the emphasis on use.

I think I can claim two qualifications for talking to you and for putting the emphasis on that side. The first qualification is that I have had the privilege of being Chairman of this Panel for just over four years—and I use the word "privilege" quite deliberately. The second is that I am not a working spectroscopist. That may seem to you to be a peculiar qualification for talking to you now, but I maintain that it is a good one, because I think it puts me in a better position to look at spectroscopy and spectroscopic methods, viewing it, as it were, from the sideline instead of from the inside, and to take the point of view of the user rather than of the investigator of spectroscopic methods.

I do not wish to under-estimate either the importance or the interest of research work of any kind. We are extremely proud of the researchers we have supporting the work of the Group and the Panel; we are also proud of the way in which the Panel works, because its method of working really means that we have the industrial spectroscopists waiting ready to adapt and adopt the methods, the instruments, and the techniques which are evolved and developed by the research workers, and we think that that is a

very good scheme. But deliberately we have not put the emphasis on research work in this symposium, for one or two reasons.

I think we should face the fact that if we were to let the research workers loose they would defeat most of us; certainly they could leave me behind. I have been in touch with their work for four years or more and still have difficulty sometimes in keeping up with their discussions. That kind of presentation might have been impressive, but I do not think it would have served the best interests of the membership of this Institute or of the applications of spectroscopy, with which we are so much concerned.

We have tried to give a fair and balanced picture of the Panel's work and outlook. We have two papers from the academic workers, whose purpose is to indicate the kind of exploratory work, the kind of long-term investigation, which must be undertaken before any sort of application can even be envisaged. Those papers, of course, do not by any means exhaust the research outlook or research activities of the Panel; but they do illustrate a rather favourite theme of mine, that in a Group or Panel of this kind the university academic workers are in an ideal position to do long-period work without paying too much regard to its ultimate practicability or direct usefulness. It is the kind of work which the spectroscopist in the industrial laboratory cannot undertake, because there the long-period work is perpetually elbowed out of the way by pressing day-to-day problems.

Next we have a paper on the suggested ideal designs of spectrometers for different purposes. I do not wish to say any more about that, except that we have present here this evening representatives of the instrument makers, and we hope that the paper will give rise to a certain amount of discussion, not too acrimonious, on the desirable features in these various designs.

The last paper is on applications purely and simply, and the point I want to stress here is that the examples quoted in the paper are actually taken from the day-to-day work of the sponsors of this Panel. They are good examples, I think, of what spectroscopic techniques can do, not in the future, but here and now, if the potentialities of the methods are appreciated.

We want spectroscopy regarded, not as something which is isolated in the research laboratory, but something which is useful, which can be brought into the control laboratory on suitable occasions, into the plant itself; we want the petroleum refiner to ask himself, is there something valuable in these techniques, am I equipped to apply the techniques, or am I running in blinkers?

That is the real message and purpose of the symposium, and that is why it is addressed primarily, not to the spectroscopic experts, but to the general body of the Institute's membership. We hope in this way to give a glimpse of what is being done and to put the main emphasis on applications. If we have misjudged the membership, the blame must rest on me; for the selection of the material put forward this evening, from the abundance of material available, the responsibility is mine.

Everybody knows how extremely pleased and privileged we are on the Panel to have the active support of Dr Thompson, F.R.S., and of his Oxford workers. I say this because we felt that, rather than ask Dr Thompson to prepare and present a more or less stereotyped paper, it

would be better to give him a sort of roving commission for about ten minutes after the papers have been presented, so that he can comment on the field which the papers have already covered or any other field that he cares to choose.

We propose to take the papers as read; the authors will highlight and present them in about ten minutes each, and we will discuss them altogether. I am not briefed on what Dr Thompson will say, but I shall not be surprised if he gives us some kind of glimpse into the future developments and applications of spectroscopy in its various ramifications.

The following papers were then presented.

THE INFRA-RED AND RAMAN FREQUENCIES OF HYDROCARBON GROUPINGS

By N. Sheppard *

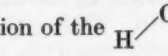
Infra-red and Raman spectra provide information about the vibration frequencies of molecules. Thus, a simple diatomic molecule such as HCl has a single vibration frequency near 2950 cm^{-1} which is observable in both infra-red and Raman spectra. This is the stretching frequency of the single linkage, and its value is determined by the masses of the two atoms and the Hooke's law force constant of the bond imagined as a spring joining them. Similarly, a bent triatomic molecule such as H_2O has three vibration frequencies, two of which are approximately in-phase and out-of-phase stretching vibrations of the O—H linkages, and one is approximately a bending vibration of the  angle as in Fig. 1. In general, a non-

Fig. 1

linear polyatomic molecule with n atoms will have $3n - 6$ such vibration frequencies and, if n is large as for most molecules with which an organic chemist deals, the number of infra-red and Raman frequencies will be considerable. For a non-cyclic molecule $(n - 1)$ of these vibrations can be described roughly as stretching modes and $(2n - 5)$ as angle-bending modes. The early work in these two branches of spectroscopy was confined mainly to the study of the spectra of the smallest molecules with a view to the identification of the various fundamental modes of vibration and the calculation of force constants. For some years now, however, the techniques have been so improved that these spectra can be obtained relatively rapidly, and hence many large molecules have been studied

* Department of Colloid Science, University of Cambridge.

whose spectra can be only partially interpreted. These spectra have, however, many qualitative and quantitative analytical applications which are of general interest to chemists. It is the purpose of the present paper to give some account of these applications, particularly those of the qualitative type, in the hydrocarbon field.

It might be asked why Raman and infra-red spectra are needed if they both give data on the fundamental vibration frequencies of molecules. The reason is that the intensities with which different vibrations occur in the two spectra depend on different factors. In the case of infra-red absorption, the intensity is a function of the magnitude of the dipole change associated with the vibration, whereas in the case of Raman scattering the intensity depends on the change in polarizability associated with the oscillation of the molecule. Thus, the stretching vibration of a homonuclear diatomic molecule will obviously, for reasons of symmetry, not give rise to a vibrating dipole and hence its vibration frequency will not occur (*i.e.*, will be forbidden) in the infra-red. On the other hand, its vibrations will give rise to an overall distortion of the electron cloud forming the bond, and at the same time of the net polarizability of the molecule. The frequency will, therefore, occur in the Raman spectrum. These two intensity conditions are thus to some extent complementary, and it often happens that a particular vibration frequency will be strong in the Raman spectra and weak in the infra-red or vice versa. Accordingly, if the maximum use is to be made of vibrational spectra for analytical purposes it is of advantage to obtain both types of spectra.

Before 1940 Raman spectra were more commonly used for analytical purposes than infra-red because of the ease with which these spectra could be semi-quantitatively obtained on the photographic plate. However, in the 1930's Professor Lecomte in Paris was pioneering the infra-red method using techniques worked out by Coblentz in 1910. During the war the value of infra-red spectroscopy for analytical purposes was more widely realized, and there followed advances in instrumentation which led to the modern recording-prism spectrometer. Much of the wartime work was done on hydrocarbons by Dr Sutherland in Cambridge and Dr Thompson in Oxford, partly under the auspices of the Institute of Petroleum, and similar work was carried out in various laboratories in the U.S.A. with the interest of the American Petroleum Institute. As a result, for versatility and ease of experimentation the infra-red method now had considerable advantages over the Raman. However, recent work in the U.S.A. by Professor Rank has led to the development of the photo-electric Raman instrument, which, with its more accurate measurement of intensities, as compared with the photographic method, is also of considerable use for hydrocarbon analytical work, at least for substances which can be obtained in the liquid state in quantities of the order of 10 cc. For this reason both infra-red and Raman data on hydrocarbons have been collected together so as to give some idea of the type of work that can usefully be undertaken with both of these techniques.

These spectra can be used for several types of analytical work. Their great usefulness arises from the large number of vibration frequencies of a polyatomic molecule. This results in very complex infra-red and Raman spectra (at least for frequencies lower than 1500 cm^{-1}) each of which is unique

for a particular molecule and has been described as its "finger-print." The spectrum as a whole can be used to establish the identity or otherwise of a substance of unknown structure with one whose infra-red or Raman spectrum has already been recorded. Alternatively, strong bands from the spectrum of a known substance may be identified in the spectrum of a mixture and used for quantitative analytical purposes. Examples of this type of application will be given in another paper.

In addition, certain chemical groupings within hydrocarbons have been found to give rise to characteristic frequencies which occur close to a particular position in the spectrum. If these are sufficiently intense they can be used to confirm or deny the presence of these groups in a substance of unknown structure. In this paper the main aim will be to give an account of these characteristic frequencies so as to illustrate the type of structural problem which can successfully be tackled by infra-red and Raman methods. It need hardly be added that many of these intense frequencies are also of much use for quantitative analytical purposes.

The characteristic features in the spectra of some of the main types of hydrocarbon groupings will be considered in turn. The data are most conveniently summarized in a series of figures, and this information is amplified with the following notes. In the construction of these figures several general procedures have been followed. The heights of the lines within the characteristic spectrum of a given group give approximate measures of their relative intensities. Intensities in different spectra are not strictly comparable, although an attempt has been made to keep a fairly uniform scale for related types of molecules whose spectra occur within the same figure. When a "characteristic" frequency is somewhat variable in position, this variability is indicated in approximate magnitude by a broadening of the base of the line (this is *not* a description of the width of the particular absorption band or Raman line). The frequency scale of the figures changes at 1800 cm^{-1}, and this is indicated by a vertical broken line through all the spectra. Characteristic frequencies of medium or strong intensity are shown between 3300 and 1500 cm^{-1}, but only strong frequencies are indicated at lower values than 1500 cm^{-1} because of the more complex nature of the spectra in this region. When possible the types of vibration associated with the different characteristic frequencies are indicated at the foot of the figure. A broken line indicates a probable correlation which has not been checked with more than a few pure substances. The frequencies quoted are those found when R (representing the remainder of the molecule) is a primary alkyl grouping, *e.g.*, ethyl, *n*-propyl, etc. When other types of substituents occur these often cause the variability of the "characteristic" frequency as indicated by the broadened base. These characteristic frequencies are often discernible in the spectra of molecules with similar structures that are not hydrocarbons, but the frequencies are liable to be more variable under these conditions and must be used with more caution.

An example 3 : 3-*Dimethylbutene*-1 (Fig. 2)

The region 3300 to 1500 cm^{-1} may be termed the "group frequency" region, as the relatively few frequencies of appreciable strength are mostly attributable to the stretching vibrations of definite hydrocarbon groupings,

viz., 3300 to 2750 cm^{-1}, C—H; 2250 to 2100 cm^{-1}, C≡C; 1700 to 1630 cm^{-1}, unconjugated C=C; 1630 to 1500 cm^{-1}, conjugated C=C, including aromatics. In a few cases abnormally strong overtone or combination frequencies in this region of the infra-red may also be used to characterize groupings as instanced later for the olefins and aromatic compounds. The region near 3000 cm^{-1} in the infra-red can most profitably be investigated with a lithium fluoride prism, as the sodium chloride prism most commonly used from 2000 to 650 cm^{-1} gives inadequate resolving power in this region.

The region 1500 to 600 cm^{-1} is usually much more complex and may be termed the " molecular finger-print " region, as almost all hydrocarbons give distinguishable spectra in this region. The skeletal stretching modes caused by vibrations of the coupled C—C linkages as well as the CH deformation (angle bending) modes occur and overlap in this region.

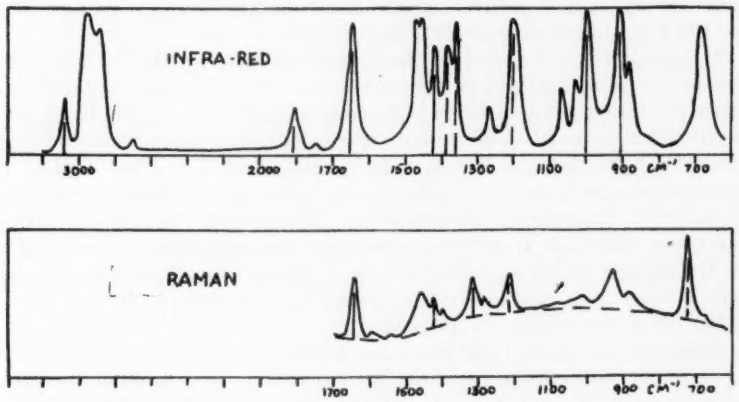


FIG. 2

INFRA-RED AND RAMAN SPECTRA OF 3 : 3-DIMETHYL BUTENE-1

Some characteristic group frequencies also occur within these limits, but these have to be of great strength to be reliably identified among the many other frequencies. Below 600 cm^{-1} the frequencies observed are mainly those involving angle-bending vibrations of the heavier carbon skeleton and are of less use for the identification of group frequencies, although they may still be used as molecular finger-prints.

Acetylenes (Fig. 3)

These have been chosen as first examples of related molecules because of their simplicity rather than because of their importance. All the three possible types of vibration (C—H stretching, C≡C stretching, and C≡C—H angle deformation) show up as characteristic frequencies in different parts of the spectra. Vibrations of the " C—R " group depend on the nature of R, and are hence not characteristic of the acetylenic part of the molecule. An abnormally strong overtone of the CH deformation (bending) mode occurs in the infra-red spectra of R—C≡C—H type molecules near 1250 cm^{-1}.

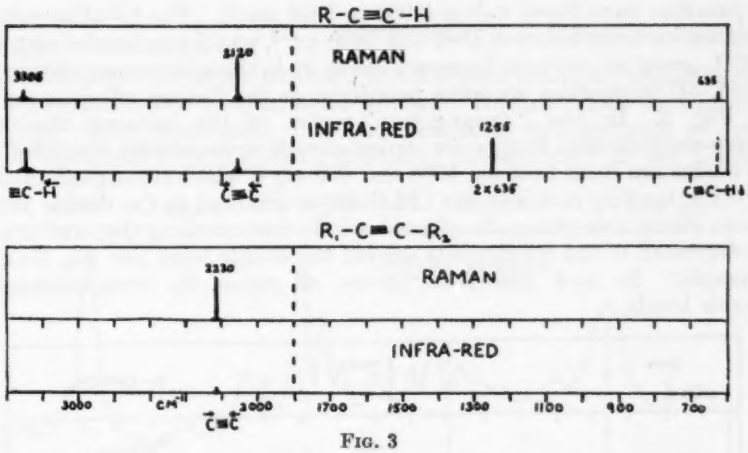


FIG. 3

CHARACTERISTIC INFRA-RED AND RAMAN FREQUENCIES OF ACETYLENES

With disubstituted acetylenes the C≡C stretching mode is the only characteristic one, and it can be seen that this can be much more reliably picked out in Raman rather than infra-red spectra.

Olefins (Figs. 4 and 5)

In the " group-frequency region " (3300 to 1500 cm^{-1}) the stretching mode of CH linkages attached to C=C groups occur in the range 3100 to 3000 cm^{-1}, and can be confused only with those of aromatic groupings which also have frequencies in this range. As noted above the CH linkages attached to C≡C groups have higher frequencies (approx 3300 cm^{-1}), whereas those

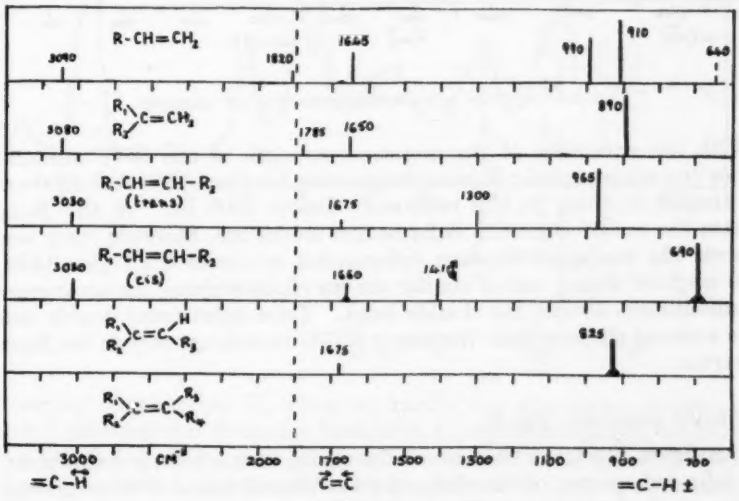


FIG. 4

CHARACTERISTIC INFRA-RED FREQUENCIES OF OLEFINS

in paraffins have lower values (3000 to 2800 cm^{-1}). The C=C stretching frequencies occur between 1700 and 1630 cm^{-1}, and for molecules with the $=CH_2$ group an overtone frequency shows up in the spectra near 1800 cm^{-1}. The C=C frequencies are more prominent in the Raman effect as shown in Fig. 5. In the "finger-print" region of the infra-red the only group-characteristic frequencies strong enough to be reliably identified for all olefins are those between 1000 and 690 cm^{-1}, which correspond to out-of-plane bending modes of the CH linkages attached to the double bond. These strong absorptions are of great use for characterizing the number and arrangement of the constituents around the double bond (see Fig. 6 as an example). No such absorption occurs, of course, for tetra-substituted double bonds.

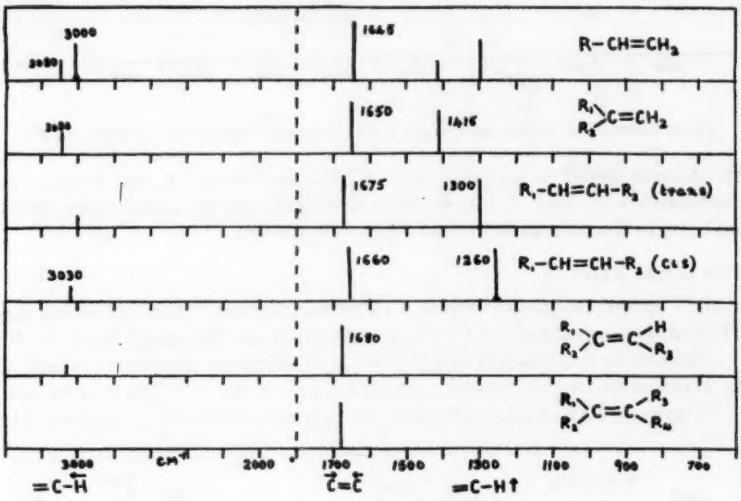


FIG. 5

CHARACTERISTIC RAMAN FREQUENCIES OF OLEFINS

With the exception of the increased strength of the C=C stretching modes the characteristic Raman frequencies between 3300 and 1500 cm^{-1} are similar to those in the infra-red. Below 1500 cm^{-1} in the Raman spectra the out-of-plane CH deformation modes are, however, very weak, whereas the analogous in-plane deformation modes in the region 1450 to 1250 cm^{-1} are strong and of similar use for characterizing the arrangement of substituents around the double bond. Tetra-substituted double bonds have a strong characteristic frequency (C=C stretching) only in the Raman spectrum.

Polymeric isoprenes (Fig. 6)

This figure illustrates the use of the strong characteristic frequencies in the infra-red spectra of the olefins for the identification of these groups in polymeric hydrocarbons. The strong absorption near 830 cm^{-1} in the spectrum of natural rubber is that of the trisubstituted double bond in the

$\left(CH_2—\overset{CH_3}{\overset{|}{C}}=CH—CH_2—\right)$ unit. In polyisoprene I, formed by emulsion polymerization of isoprene, this band is still of great strength, corresponding to a predominantly 1 : 4 addition process. Weaker bands *ca* 910 and 890 cm^{-1} show that some 1 : 2 polymerization has occurred to give $—CH=CH_2$ and $—C(CH_3)=CH_2$ groupings respectively. In the sodium

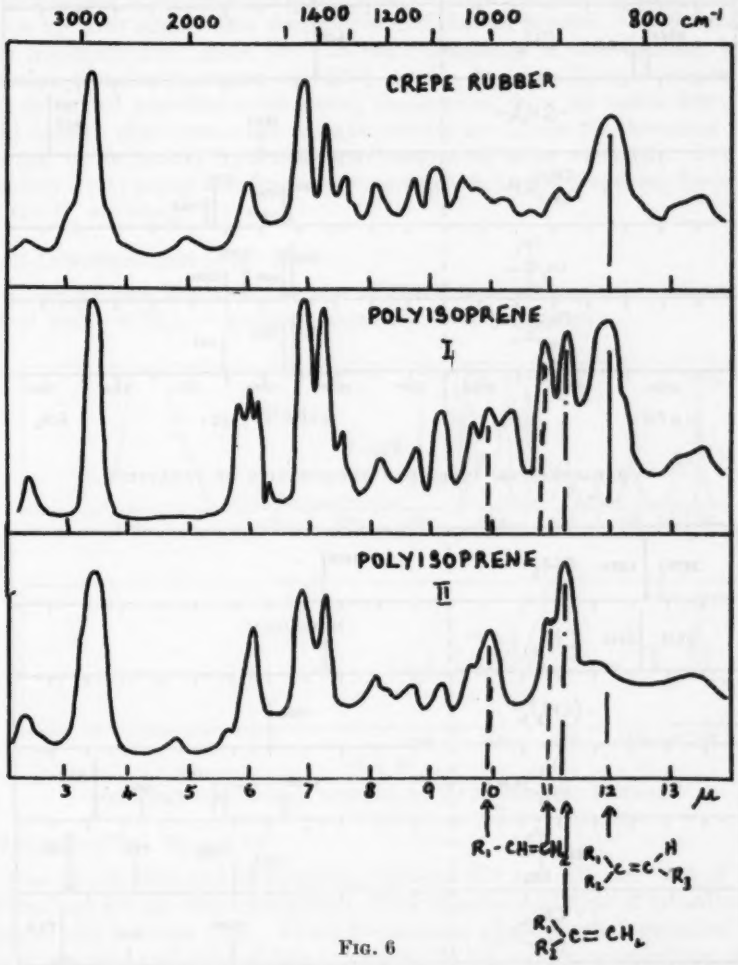


FIG. 6

polymerized polyisoprene II, however, hardly any absorption occurs near 830 cm^{-1}, showing that there has been little 1 : 4 polymerization, whereas a strong broad absorption near 900 cm^{-1} shows that both types of double bond arising from 1 : 2-type addition are present in high concentration. Similar conclusions can be reached from a study of the C=C frequencies between 1600 and 1700 cm [1].

Paraffinic groupings (Figs. 7 and 8)

The characteristic frequencies of the CH_3 and CH_2 groups occur strongly in most hydrocarbon spectra. The strong infra-red absorption at 725 cm^{-1}

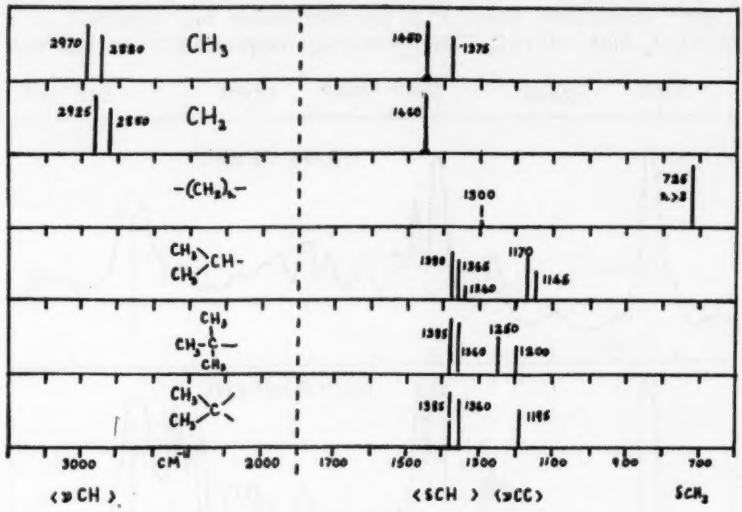


FIG. 7

CHARACTERISTIC INFRA-RED FREQUENCIES OF PARAFFINS

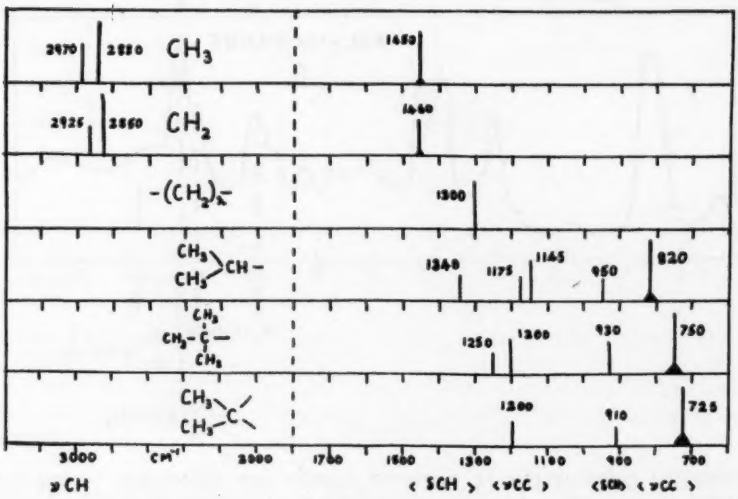


FIG. 8

CHARACTERISTIC RAMAN FREQUENCIES OF PARAFFINS

for $-(CH_2)_n-$ groups occurs in this position only when $n>3$. For $n = 2$ and $n = 1$ (as for *n*-propyl or ethyl groups) this absorption shifts to

740 and 770 cm^{-1} respectively. In the infra-red spectra of the branched paraffins the symmetrical methyl deformation frequency at 1375 cm^{-1} for a lone methyl group splits into two components due to interaction of the neighbouring methyl groups as shown in the figure. The isolated absorption at 1340 cm^{-1} in the spectrum of the *iso*propyl group is caused by the CH deformation mode of the lone CH linkage.

The strong infra-red absorptions near 1375 cm^{-1} of methyl groups do not show up with appreciable strength in the Raman spectra. In the case of the polymethylene chain the 725 cm^{-1} frequency is also missing, but a Raman frequency occurs at 1300 cm^{-1}. In the Raman spectra of the branched paraffins some strong frequencies show up below 850 cm^{-1}, and despite their somewhat variable nature are of use for detecting these groups in saturated hydrocarbons because of their strength. For the tertiary butyl group this frequency corresponds to the breathing frequency of the C_5 skeleton.

2 : 2-*Dimethylhexane* (Fig. 9)

These spectra illustrate the use of characteristic frequencies of tertiary butyl and $—(CH_2)_n—$ groups to identify these groupings.

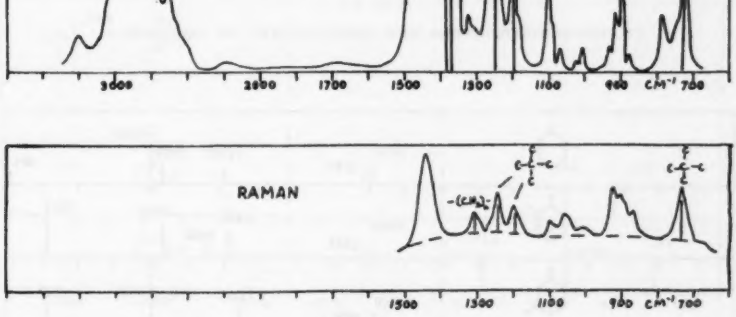


FIG. 9

INFRA-RED AND RAMAN SPECTRA OF 2 : 2-DIMETHYL HEXANE

Aromatics (Figs. 10 and 11)

The strong infra-red absorptions between 870 and 670 cm^{-1} are of particular use for the characterization of the number and type of substituents around the benzene ring. These frequencies are somewhat variable, and for the mono- and disubstituted compounds the values recorded are those for primary alkyl substituents, *e.g.*, ethyl groups. Methyl substituents usually cause slightly lower values, and *iso*propyl and tertiary butyl substituents higher values. The series of relatively weak absorptions between 1950 and 1750 cm^{-1} occur in clear regions of the spectra and form patterns of bands which are useful for confirming the number and arrangement of benzene ring substituents. They are not fundamentals.

Less complete experimental data are available for the Raman spectra,

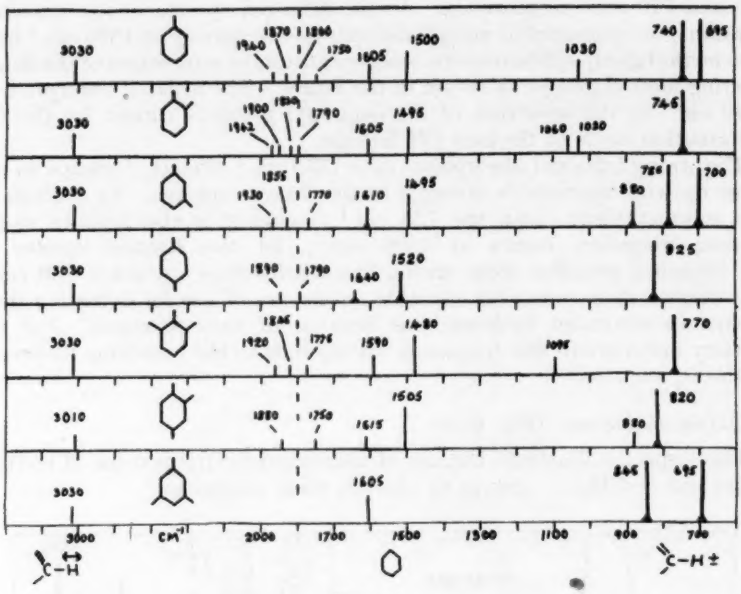


FIG. 10

CHARACTERISTIC INFRA-RED FREQUENCIES OF AROMATICS

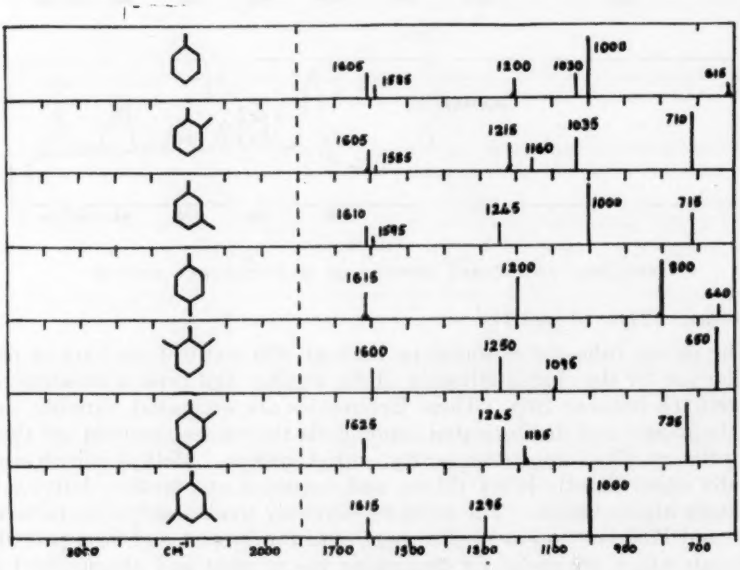


FIG. 11

CHARACTERISTIC RAMAN FREQUENCIES OF AROMATICS

but it can be seen that they form a useful adjunct to the infra-red data for characterizing the substitution pattern.

Naphthene hydrocarbons (Figs. 12 and 13)

Several infra-red frequencies exist which can be used to characterize hydrocarbons with singly substituted three-, four-, five-, and six-membered saturated rings. With the exception of the substituted *cyclo*propanes,

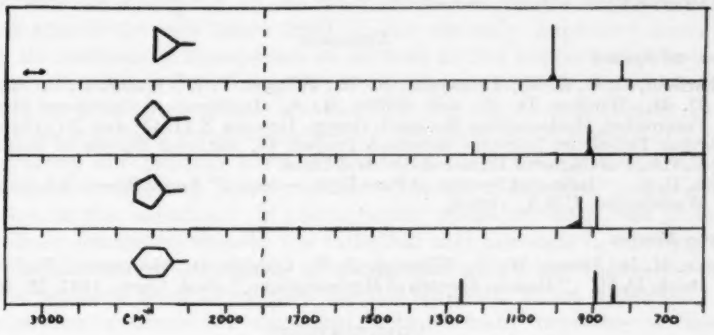


FIG. 12

CHARACTERISTIC INFRA-RED FREQUENCIES OF NAPHTHENES

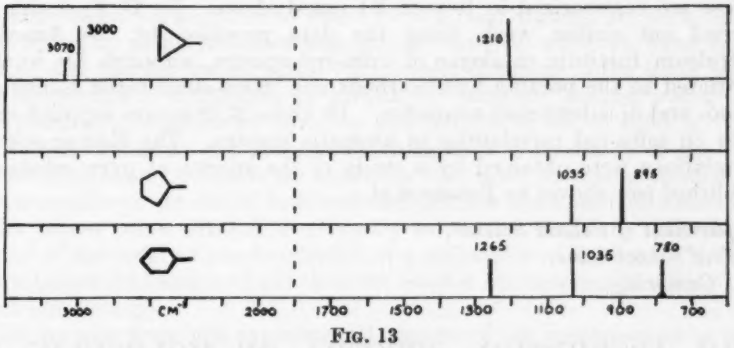


FIG. 13

CHARACTERISTIC RAMAN FREQUENCIES OF NAPHTHENES

however, these are of poor strength and the Raman spectra are more useful for this purpose. Insufficient data are available for the drawing up of similar rules for more heavily substituted rings. The CH_2-stretching frequencies in the rings differ little from those in ordinary saturated hydrocarbons. An exception is the *cyclo*propane ring, whose CH_2 modes have abnormally high values.

It can be concluded that, given a sufficient range of pure substances, infra-red and Raman spectra will provide the means to characterize nearly all the common structural groupings in hydrocarbons.

However, a final work of caution is perhaps needed in that the data are presented in Figs. 2 to 13 in a very simplified form. These summaries are

intended as guides to some of the important information to be found in the literature, but the detailed spectra themselves should be consulted in order to obtain a more complete impression of the ease or otherwise with which the individual characteristic frequencies may be distinguished. Furthermore, much more accurate use can be made of the spectroscopic data when these are considered in conjunction with chemical evidence for the structure of molecule or substance in question than when conclusions are drawn from the spectra alone.

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Infra-red Spectra

Sutherland, G. B. B. M., Thompson, H. W., Fellgett, P. B., Harris, G. P., Simpson, D. M., Whiffen, D. H., and Willis, H. A. Institute of Petroleum Research Committee, Hydrocarbon Research Group, Reports X (1945) and XI (1946).

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Raman Spectra

Fenske, M. R., Braun, W. G., Wiegand, R. V., Quiggle, D., McCormick, R. W., and Rank, D. H. "Raman Spectra of Hydrocarbons," *Anal. Chem.*, 1947, **19**, 700–65.

Correlations

Most of the correlations of the infra-red spectra were made as part of the wartime compilation of spectra by Dr Sutherland and Dr Thompson. These are summarized in Report XI noted above. Dr D. C. Smith has carried out similar work, using the data provided by the American Petroleum Institute catalogue of infra-red spectra, although his work is restricted to the paraffin hydrocarbons and mono-substituted olefins and mono- and di-substituted aromatics. Dr Delia M. Simpson supplied extra data on infra-red correlations of aromatic spectra. The Raman spectra correlations were obtained by a study of the spectra of pure substances published (see above) by Fenske *et al.*

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THE ABSORPTION SPECTRA OF MOLECULES IN THE VACUUM ULTRA-VIOLET

By W. C. Price *

The extension of the methods of absorption spectroscopy from the visible region of the spectrum to long wavelengths into the infra-red and to short wavelengths into the ultra-violet has resulted in a great increase in our knowledge of the structure of molecules, and has been accompanied also by a development of these regions for the purposes of analytical spectrophotometry. It is natural that at the present time we should be trying to extend our observations still farther into the infra-red and farther into the ultra-violet, and we shall be concerned in what follows with the spectro-

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scopy of the region below 2000 Å, *i.e.*, below the region normally accessible with quartz spectrographs.

The experimental difficulties which set a short-wave limit of 2000 Å to the normal practice of spectrography are of three kinds. The first is that the oxygen present in the air absorbs strongly at short wavelengths. This means that the whole of the light path, including the spectrograph, has to be evacuated to pressures of a few hundredths of a mm. The second factor arises from the absorption of the material of the prism. Nearly all substances absorb strongly below 2000 Å, and the only dispersive materials which are sufficiently transparent to be used in this region turn out to be calcium and lithium fluorides. Even with these materials the short-wave limit set by their transmission is about 1200 Å. To work at shorter wavelengths the spectrum must be formed by reflection at the surface of a concave grating, and gratings have been used to cover the whole wavelength range down to the long X-ray regions. The third difficulty arises in the detection of the radiation. If photographic plates are used, the gelatine of ordinary emulsions absorbs the radiation and prevents it reaching the silver halide grains. Specially prepared plates having extremely low gelatine contents have to be used for the spectrum to be registered. If photo-electric methods are employed it is generally necessary to use a fluorescent screen in front of the photo-cell, since the envelope of the multiplier is opaque to the radiation and prevents it reaching the photo-cathode. However, some photo-multipliers with thin fused-quartz windows are now available which are sensitive to about 1550 Å, and argon-filled photo-cells with platinum photo-cathodes and lithium fluoride windows have been used at still shorter wavelengths. Hydrogen discharge tubes have been used to provide a background of continuous radiation against which the absorption can be observed down to wavelengths of about 1650 Å. To make observations at still shorter wavelengths it is necessary to use the Lyman continuum, which is an explosive condenser discharge through a narrow capillary. It should be mentioned that the absorption of molecules in the region below 2000 Å is generally so intense ($\log \varepsilon \sim 5$) that path-lengths of the order of one-hundredth of a millimetre of the gas at N.T.P. or equivalent thicknesses of solutions are all that are necessary to bring the bands out strongly.

Turning now from the experimental aspects of the spectroscopy of the vacuum ultra-violet, the nature of the spectra observed in this region will be considered. First it is important to understand that light of wavelength 2000 to 500 Å corresponds to photons of energies from 6 to 24 electron volts or 140 to 560 cal/mol. Photons of these energies are able to excite the electrons of molecules to very high orbits and in some cases completely to remove them from the molecule, *i.e.*, to photo-ionize the molecule. In atoms this photo-ionization is observed as a series of lines corresponding to excited orbits of increasing size and principal quantum number. These lines gradually weaken and get closer together on going towards shorter wavelengths. Eventually they converge together towards a limit from which a region of continuous absorption starts. This corresponds to the photo-ionization of the atom, and a similar process is to be expected for molecules. In molecules, however, every electronic transition is usually accompanied by vibrational changes, and a pattern of bands

replaces each line of the atomic analogue. The situation is further complicated by the fact that a breaking of the bonds of a molecule by photodissociation sometimes occurs. The result of this is to reduce the sharpness of the bands, an effect which may vary from giving just a slightly diffuse character to the bands to replacing whole regions by continuous featureless absorption.

While only relatively complicated molecules have absorption spectra in the range above 2000 Å, all molecules show regions of absorption at shorter wavelengths. Methane, for example, starts to absorb around 1250 Å, ethane at 1350 Å. Unfortunately all saturated hydrocarbons have only diffuse absorption spectra, and it is for unsaturated ones only that Rydberg series of patterns analogous to those of atomic spectra are observed. The spectra of acetylene and ethylene are good examples of molecules with relatively sharp spectra of the Rydberg type described in the preceding paragraph. These start with sets of bands at about 1520 Å and 1750 Å respectively, followed on the short-wavelength side by other similar sets of bands which get weaker and closer together, eventually fusing into a photo-ionization continuum at wavelengths corresponding to 11·41 and 10·47 V respectively. These values agree with the determinations of the ionization potentials of these molecules by electron-impact methods, though the spectroscopic ionization potentials are of a higher order of accuracy. The interpretation of the spectrum shows them to correspond to the excitation and subsequent removal of the double-bond (π) electrons. When double bonds are conjugated theory shows that the electrons split up into two or more groups of different ionization potentials from that of an unconjugated bond. Some of these groups have relatively higher and some relatively lower ionization potentials, although on the whole there is, of course, an increase in the binding energy of the molecule. The result is that the bands corresponding to the excitation of the electrons of the lower ionization potential are shifted towards longer wavelengths. Thus the first strong bands of butadiene, for instance, appear at *ca* 2150 Å and those of hextriene at *ca* 2500 Å. The minimum ionization potentials of these molecules are reduced to values of 9·07 and *ca* 8·3 V relative to the value 10·47 V for ethylene. The longer wavelength bands which are found for a molecule do not generally correspond to atomic-like excitation of a Rydberg type, but are most frequently to be interpreted as intra-valence shell transitions, that is transitions in which the electron does not change its principal quantum number but jumps from an orbit in which it is bonding to one in which it is anti-bonding.

The short-wave spectrum of benzene has been studied, and it has been found to show a set of atomic-like bands in the region below 1700 Å. The analysis of these bands has permitted the very accurate value of 9·24 V to be obtained for the ionization potential of benzene. The detailed study of the spectrum has given valuable information which helps in our understanding of the electronic structure of this important molecule in terms of the quantum theory. The longer wavelength bands of benzene and its derivatives have been interpreted in terms of transitions of an intra-valence shell type.

The addition of alkyl groups to a molecule has the effect of shifting its absorption spectrum to longer wavelengths, of making its bands more

diffuse, and of reducing its ionization potential. This may be related to the effect of solvents and high pressures on the spectra of the absorbing units or chromophores. It may be of importance in studying the influence of these factors on the activation energies required to bring about certain chemical reactions. The position of the alkyl groups with respect to the chromophores is often important in determining the magnitude of the effect on its absorption spectrum. Thus the spectra of hydrocarbons with a *cis*-substituted double bond have spectra which generally fall to the long-wavelength side of the corresponding compound in which the substitution is in the *trans* position. Many simple molecules which give rise only to diffuse regions of continuous absorption in the near ultra-violet, have sharp, well-defined spectra in the vacuum ultra-violet. Amongst these are the following: water, hydrogen sulphide, methyl alcohol, methyl mercaptan, formic acid, aldehydes, ketones, the alkyl halides, the halogen acids, etc. To obtain sharp bands these substances must generally be investigated in the vapour state, as the orbits to which the electrons are excited by the short-wave radiation are of such large dimensions that they would be seriously affected by solvent or other molecules if investigated as liquid.

While it is doubtful whether the short-wave region of the spectrum will be of great value for analytical purposes except in special cases, there is no question that it has been of great importance in elucidating the electronic structure of the simpler molecules in terms of modern theory. For the benefit of those who wish to pursue the subject farther, a list of references to review articles on the subject is appended.

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INDUSTRIAL APPLICATIONS OF ABSORPTION SPECTROSCOPY

By the Spectroscopic Panel of the Hydrocarbon Research Group of the Institute of Petroleum

Introduction

Absorption spectroscopic methods have now been developed to such an extent that they can be satisfactorily applied to industrial problems. The petroleum industry as much as any has been responsible for the industrialization of a branch of science, investigations on which until the outbreak of the last world war were mainly confined to the research laboratories of universities and technical institutions. That spectroscopy has found such wide application in the petroleum and chemical industries is hardly surprising when it is realized that a spectrum is truly a fundamental property of a material.

This paper deals very briefly with the basic principles and then describes a few varied applications of an industrial nature.

Basic Principles

The wavelengths at which a compound exhibits absorption and the extent of the absorption are governed by its molecular structure, and it is this selective absorption that forms the basis of all analytical work, both qualitative and quantitative.

In the ultra-violet region (approximately 2000 to 4000 Å) of the spectrum certain types of materials only exhibit selective absorption. Of the hydrocarbons, aromatics, naphthalenes, and conjugated diolefins have characteristic absorption, while saturated hydrocarbons, both paraffinic and naphthenic, may be regarded as being transparent.

Infra-red radiation, on the other hand, is absorbed by almost all gases, liquids, and solids, and the absorption is highly selective, certain wavelengths being strongly absorbed while closely adjoining ones are not. The frequencies of infra-red radiation absorbed are equal to the vibrational frequencies of the atoms within the molecules. These depend on the masses of the atoms in the molecule, the inter-atomic forces (bond strengths) and distances, and are unique for each molecular species. The infra-red absorption spectrum of a compound is thus a unique pattern or " finger-print " characteristic of that substance, and this leads to its use in identifying compounds. The spectrum of the unknown may be compared with published spectra or with the spectra of likely materials recorded on the same instrument.

On the other hand, as the infra-red spectrum of a material is entirely dependent on its molecular structure, materials of similar type do in fact possess certain similarities in their spectra. These similarities can be very useful, for in certain problems where a complete individual compound analysis is not possible owing to the complexity of the mixture an estimate of certain types present can be obtained, *e.g.*, olefins and aromatics. Moreover, infra-red spectroscopy can be usefully applied to the problem of molecular structure (as already shown in Dr Sheppard's paper), in that the presence of certain bonds or groups in a molecule is usually accompanied by absorption bands at certain wavelengths. The examination of the infra-red spectra of a large number of substances has shown that certain bands can be attributed to vibrations occurring mainly in particular bonds or groups in the molecule. It is thus possible to draw up a chart (Fig. 1) giving the approximate frequencies associated with particular bonds or groups and to use this as a basis of qualitative analysis in establishing their presence in a substance being examined. A rough classification of these localized frequencies into valence frequencies (motion occurring mainly along a bond) and deformation frequencies (motion occurring mainly perpendicular to a bond) has been adopted. The frequency associated with a particular bond or group is, however, affected to a certain extent by the nature of the rest of the molecule. For example, the frequency of the valence vibration of the carbonyl group is slightly different in anhydrides, esters, carboxylic acids, and aldehydes and ketones.

For frequencies greater than about 1400 cm^{-1} the bands observed in a spectrum can be assigned to a particular group or to one out of two or three

possibilities (although weak bands in this region may be due to overtones or combinations of other bands). For example, all compounds containing the S–H group have an absorption band near 2450 cm^{-1}, and the presence of a band at this frequency in the spectrum of an unknown compound is strong evidence for the presence of a S–H group. On the other hand, for frequencies below about 1400 cm^{-1} many of the bands are due to vibrations involving all the atoms of a molecule rather than those of a particular part or group; consequently, an observed frequency cannot be definitely assigned to a particular group, even though this group is known to have the same frequency as that observed. For example, all compounds containing the *iso*propyl group have an absorption band near 1170 cm^{-1}, but the presence of a band at this frequency in the spectrum of an unknown compound cannot be taken as establishing the presence of an *iso*propyl group, since a non-localized vibration of the whole molecule may give rise to a band at this frequency.

The correlations given in the chart have been derived from a study of the spectra of the liquids, and many of the bands show shifts with change of state. Thus in the spectrum of acetone vapour the carbonyl absorption band lies at 1740 cm^{-1}, while for liquid acetone it lies at 1720 cm^{-1}.

It must be emphasized that the information given in the chart is presented in a much simplified form; the detailed application of the correlations given requires considerable experience and knowledge of the finer points. The use of this chart by an inexperienced worker is just as likely to lead to a " howler " as to the true structure of the compounds concerned.

Quantitative absorption analysis in the ultra-violet and infra-red is based on two fundamental laws relating the intensities of the light incident on and transmitted by the sample. The first, due to Lambert, states that the proportion of radiation absorbed by a substance is independent of the intensity of the incident radiation, while Beer's Law states that the quantitative absorption depends on the number of absorbing molecules in the path of the radiation. Combining the two therefore dI (the intensity absorbed by a small layer of absorbing material) is proportional to I (the intensity of radiation incident on it), and also,

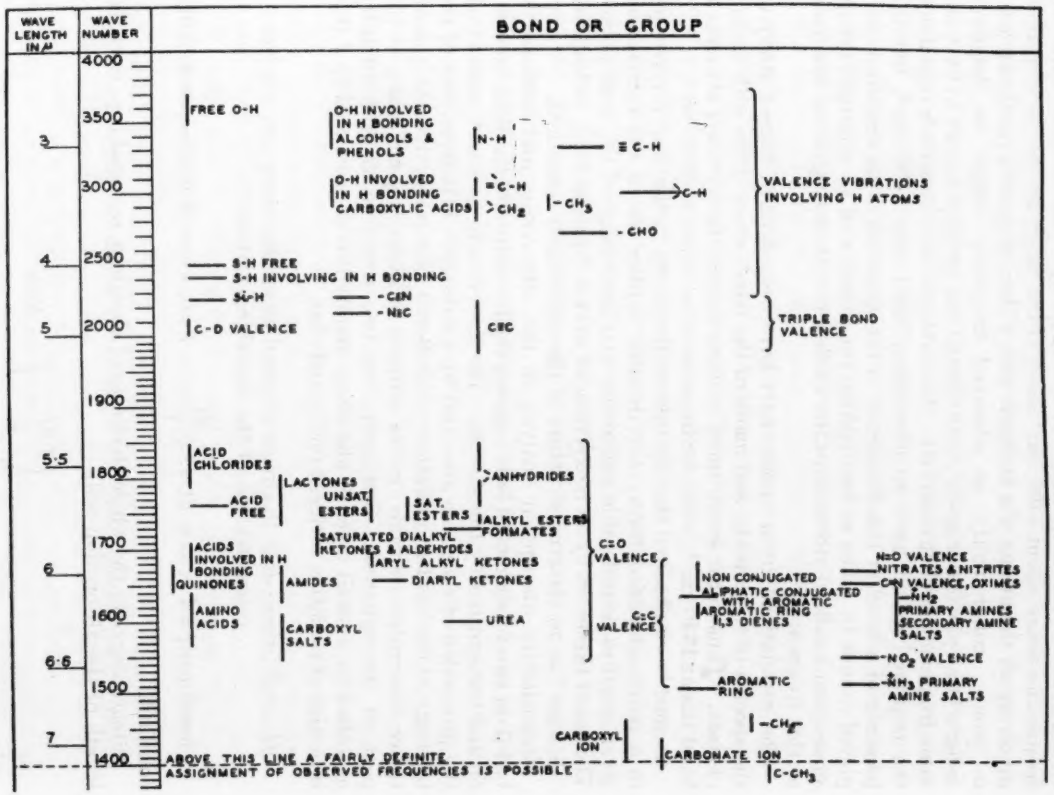
$dI \propto c\,dt$ (where dt is thickness of small absorbing layer and c is the concentration of the absorbing material).

Therefore $dI \propto I \times c \times dt$, *i.e.*, $\frac{dI}{I} = -Kcdt$, where K is a proportionality constant.

Integrating over the whole thickness of absorbing material (*i.e.*, over the length of the absorption cell)

$$\int_{I_0}^{I_T} \frac{dI}{I} = \int_0^t -Kcdt$$

i.e., $\log \frac{I_0}{I_T} = Kct$ where I_0 and I_T are the intensities of the incident and transmitted energies. $\log \frac{I_0}{I_T}$ is known as the optical density or absorbance (d).


WAVE LENGTH IN μ
WAVE NUMBER
BOND OR GROUP
4000
3500
3
3000
4
2500
5
2000
1900
5·5
1800
1700
6
1600
6·6
1500
7
1400
FREE O-H
O-H INVOLVED IN H BONDING ALCOHOLS & PHENOLS
O-H INVOLVED IN H BONDING CARBOXYLIC ACIDS
N-H
=C-H
>CH2
≡C-H
-CH3
=C-H
-CHO
VALENCE VIBRATIONS INVOLVING H ATOMS
S-H FREE
S-H INVOLVING IN H BONDING
Si-H
-C≡N
-N=C
C-D VALENCE
C≡C
TRIPLE BOND VALENCE
ACID CHLORIDES
ACID FREE
LACTONES
UNSAT. ESTERS
SAT. ESTERS
>ANHYDRIDES
ALKYL ESTERS
FORMATES
SATURATED DIALKYL KETONES & ALDEHYDES
ARYL ALKYL KETONES
DIARYL KETONES
UREA
ACIDS INVOLVED IN H BONDING
QUINONES
AMIDES
AMINO ACIDS
CARBOXYL SALTS
C=O VALENCE
C=C VALENCE
NON CONJUGATED
ALIPHATIC CONJUGATED WITH AROMATIC
AROMATIC RING
1,3 DIENES
AROMATIC RING
N=O VALENCE
NITRATES & NITRITES
C=N VALENCE, OXIMES
-NH2
PRIMARY AMINES
SECONDARY AMINE SALTS
-NO2 VALENCE
-NH3 PRIMARY AMINE SALTS
-CH2-
CARBOXYL ION
CARBONATE ION
C-CH3
ABOVE THIS LINE A FAIRLY DEFINITE ASSIGNMENT OF OBSERVED FREQUENCIES IS POSSIBLE

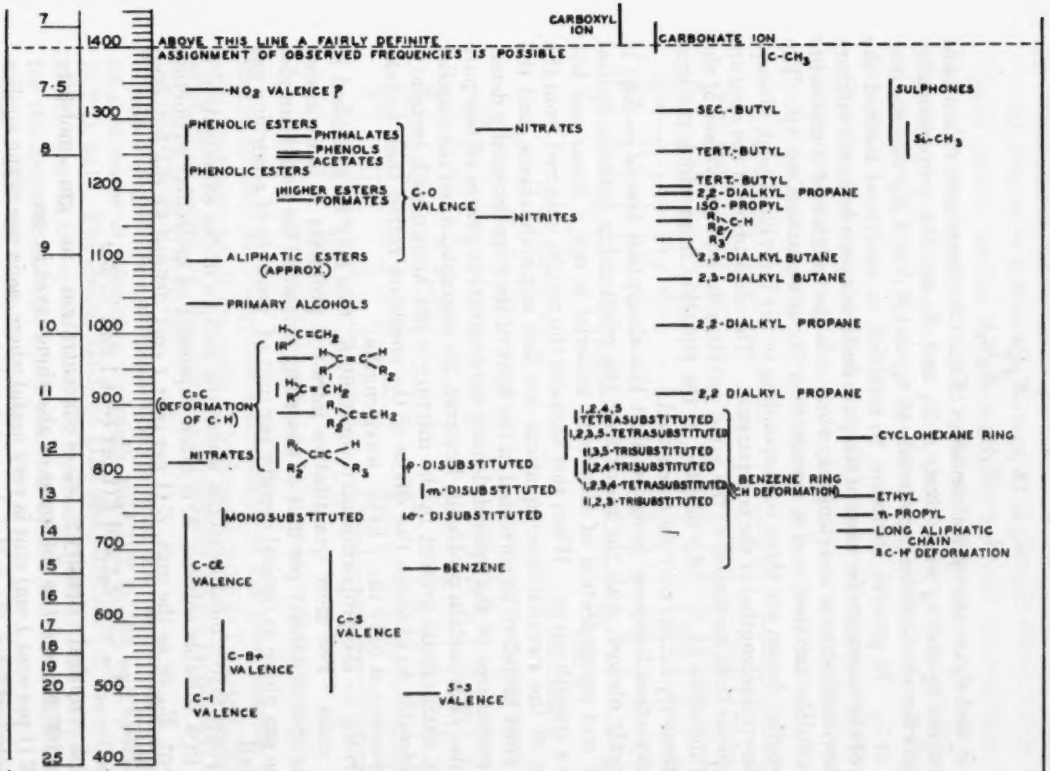


FIG. 1 CHARACTERISTIC INFRA-RED ABSORPTION BANDS

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Furthermore, the absorption, expressed as optical density, of a mixture of substances at any wavelength is the sum of the optical densities of the components at that wavelength, provided, of course, that no interaction takes place between them. Therefore expressed mathematically for a mixture of two components the following relationships are obtained :—

$$d_1 = (K_1c_1 + K_2c_2)t$$
$$d_2 = (K_1^1c_1 + K_2^1c_2)t$$

where d_1 and d_2 are the optical densities of the two-component mixtures at wavelengths λ_1 and λ_2 respectively : K_1 and K_2 are the proportionality constants for the absorbing materials at λ_1, and K_1^1 and K_2^1 are the constants at λ_2. In general, therefore, to establish an analytical method the values of the constants for each of the pure materials present in the mixture must be obtained at n wavelengths, where n is the number of components present in the mixture, and a system of n linear equations set up. The wavelengths chosen are those corresponding to the individual peak absorptions (key wavelengths) of the components. The absorption of the mixture or sample is then measured at the same wavelengths and the values of the optical densities ($d_1 \ldots d_n$) inserted in the equation from which the concentrations ($c_1 \ldots\ldots c_n$) may be calculated.

It very often happens, however, that the absorption law ($d = Kct$) is not strictly obeyed, with the result that the relationship between optical density and concentration of absorbing material is not a linear one but follows a smooth curve. When this happens the results obtained from the solution of the simultaneous equations are first approximations, and the results must therefore be corrected in the light of the experimentally determined curvatures of the optical density/concentration curves of the pure materials. For certain problems, however, for example, when the number of likely components present in the mixture is not known with certainty, it is preferable to examine the whole of the spectrum rather than to take measurements at only the " key " wavelengths.

Returning to the proportionality constant K, this may be expressed in various units. For most quantitative infra-red problems K is expressed either as optical density per unit of absorbing thickness for liquid samples or in the gas phase as optical density per unit of pressure of absorbing gas in the cell.

For quantitative measurements where the sample under examination is diluted in a suitable solvent, K is often expressed as molecular extinction coefficient, E_m, or as the unit, E (1 per cent 1 cm), defined by the following equations :—

$$E_m = d/c_m t \text{ and } E(1 \text{ per cent } 1 \text{ cm}) = dc_g t$$

where d = optical density; c_m = concentration in gm mol/litre; c_g = gm/100 ml, and t = thickness of absorbing layer in cm.

The E (1 per cent 1 cm) unit is very useful where, as in one of the applications described later, the molecular weight of the material is not known.

Further details of the methods and techniques of both qualitative and quantitative spectroscopic absorption analyses are given in the scientific literature.[1-10]

It will be realized from the above that pure materials are essential for spectrometer calibration. The Chemical Research Laboratory, Tedding-

ton, have undertaken to supply pure hydrocarbons, and a list of those already available is attached as an appendix.

Applications

(1) *Detection and Determination of Small Amounts of Hydraulic Fluid D.T.D. 641 Present in a Mineral Oil, such as Hydraulic Fluid D.T.D. 585*

Since current service requirements call for both mineral-base (D.T.D. 585) and castor-base (D.T.D. 641) hydraulic fluids for aircraft with synthetic and natural rubber glands and seals, respectively, the possibility of difficulties caused by mixing these two incompatible fluids has always to be considered.

Chemical and visual methods are adequate to detect gross contamination of a mineral oil by a vegetable oil, but hitherto it has not been possible to detect a minute amount of vegetable oil in a mineral oil. However, by

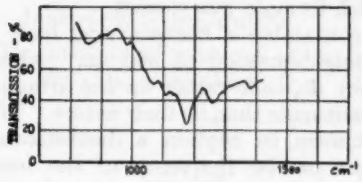


FIG. 2
PURE CASTOR OIL

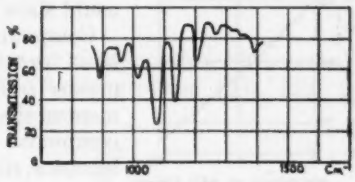


FIG. 3
PURE CELLOSOLVE

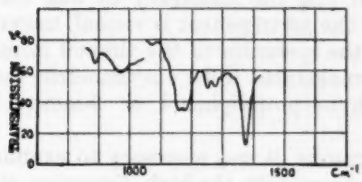


FIG. 4
HYDRAULIC FLUID, D.T.D. 585

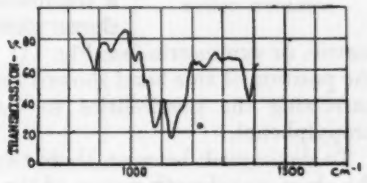


FIG. 5
HYDRAULIC FLUID, D.T.D. 641

means of infra-red absorption spectroscopy it has been possible to detect and determine small amounts of hydraulic fluid D.T.D. 641, which is a mixture of castor oil and cellosolve (ethylene glycol monoethyl ether) in the mineral oil D.T.D. 585.

Figs. 2–5 give the absorption spectra from 800 cm^{-1} to 1500 cm^{-1} (7μ to 14 μ) of castor oil, cellosolve, hydraulic fluid D.T.D. 585, and hydraulic fluid D.T.D. 641. The strong bands at 1138 and 1078 cm^{-1} of the cellosolve are clearly seen in the spectrum of the hydraulic fluid D.T.D. 641, and in fact for the determination of small amounts of D.T.D. 641 in D.T.D. 585 the band at 1078 cm^{-1} has been used.

For the quantitative determination the working curve, Fig. 6, correlating per cent transmission at 1078 cm^{-1} with per cent D.T.D. 641 in the mixture, was constructed from an examination of known blends of D.T.D. 641 and D.T.D. 585.

The estimated accuracy of the method, based on the accuracy with which it was possible to measure per cent transmission with the instrument used

for this work, is $\pm 0{\cdot}02$ per cent, and the lowest amount of D.T.D. 641 which can be detected with certainty is considered to be 0·05 per cent.

As the quantitative method is really based on measuring the percentage transmission at the frequency of the cellosolve band and not of the castor oil, it cannot be used for a hydraulic fluid which is a mixture of castor oil with some other diluent, although a similar technique might be feasible, provided there is a considerable difference in the absorption spectra of the two fluids.

(2) *Identification of a Thymol Isomer*

A thymol isomer, prepared by the propylation of *m*-cresol, could be either 3-methyl-2-propylphenol (vicinal), 3-methyl-4-propylphenol (unsymmetric), 3-methyl-5-propylphenol (symmetric), or 3-methyl-6-propylphenol (unsymmetric). The infra-red spectrum of the compound was recorded in order to see if it could show which formula was correct.

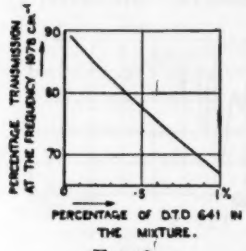


FIG. 6

WORKING CURVE

Compounds containing a benzene ring have a band in the neighbourhood of 800 cm^{-1} whose precise frequency depends rather on the arrangement of the substituents than on their nature. If a compound is known to contain a disubstituted benzene ring the precise frequency of the band shows whether the substituents are arranged *ortho*, *meta*, or *para*; similarly, if it is known to contain a trisubstituted ring the frequency of this band shows whether the arrangement is vicinal, unsymmetric, or symmetric (see Fig. 1). In the spectrum of the thymol isomer the position of this band showed the arrangement to be unsymmetric, thus narrowing the possibilities to 3-methyl-4-propylphenol or 3-methyl-6-propylphenol.

To distinguish between these two formulæ, it was necessary to examine the short-wavelength region of the spectrum with the high dispersion of a lithium fluoride prism. In the liquid state alkylphenols have a broad band at 3000 to 3300 cm^{-1} due to the valence vibration of the –OH group involved in hydrogen bonding; in dilute solution in a non-polar solvent such as carbon tetrachloride this band is replaced by a sharp one at 3620 cm^{-1} due to the valence vibration of an unassociated –OH group; the wave-number difference between the two bands is a measure of the strength of the intermolecular hydrogen bonds. It seemed probable that the strength of the intermolecular hydrogen bonds in alkylphenols depends on the number and size of the alkyl groups *ortho* to the hydroxyl group, so the spectra of thirty-one alkylphenols were recorded in both the pure state and in dilute solution, and the wave-number differences between the broad and sharp bands were measured. The results obtained, summarized in Table I, show that the strength of the hydrogen bonds does in fact depend on the *ortho* substituents.

For the thymol isomer the wave-number difference between the liquid and the dilute solution was 280 cm^{-1}, so there are no substituents *ortho* to the hydroxyl. The compound is thus 3-methyl-4-propylphenol and not 3-methyl-6-propylphenol.

Since this work was carried out similar results to those given in the table above have been reported elsewhere.[11, 12]

TABLE I

Effect of Benzene Substitution on Hydrogen Bonding

Substituents *ortho* to hydroxyl	Wave no. difference between pure liquid and dilute solution	No. of compounds examined
None	300–250 cm^{-1}	6
One small (methyl or ethyl)	230–150 cm^{-1}	8
Two small	110 cm^{-1}	2
One large (butyl or octyl)	130– 90 cm^{-1}	10
One large and one small	130– 90 cm^{-1}	3
Two large	10 cm^{-1} *	2

* Both bands are sharp, steric hindrance prevents hydrogen bonding.

(3) *Analysis of Nitroparaffins*

The analysis of mixtures of the four lowest nitroparaffins, nitromethane (b.p. 101° C), nitroethane (b.p. 114° C), 2-nitropropane (b.p. 120° C),

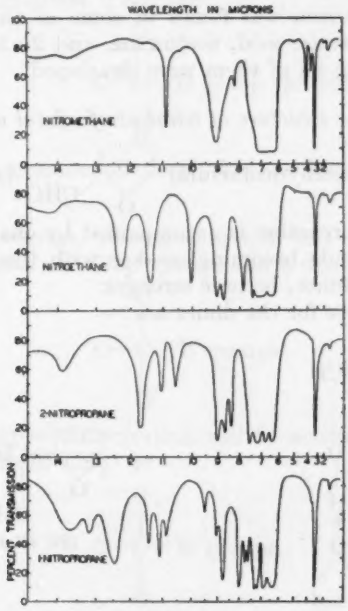


FIG. 7

INFRA-RED TRANSMISSION CURVES FOR FOUR LOWEST NITROPARAFFINS

(Nielson, J. R., and Smith, D. C. *Indust. Engng Chem. Anal.*, 1943, **15**, 610)

and 1-nitropropane (b.p. 131° C) is an important application of infra-red spectroscopy, as no satisfactory alternative method is available for mixtures of more than two of them.

The mixtures analysed were mainly fractions from the stills on the plant, and the analyses were needed for still control; in addition, samples of pure nitroparaffins were tested for purity before despatch, and crude products from the nitration of propane were analysed.

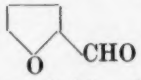
Fig. 7 shows part of the infra-red spectra of the four nitroparaffins from which the key bands were chosen. That for nitromethane is at 10·9 μ; nitroethane and 2-nitropropane do not absorb at this frequency, but allowance must be made for the weak absorption of 1-nitropropane. However, since nitromethane and 1-nitropropane differ most in boiling point they do not often occur together.

Nitroethane has key bands at 11·5 μ and 10·05 μ, none of the other constituents absorbing at these wavelengths. It can also be estimated using the bands at 12·5 μ and 8·0 μ if no 1-nitropropane is present. As many bands as possible should be used in an analysis, as the accuracy obtainable is thereby increased; apart from the purely statistical effect there is a check on the presence of impurities.

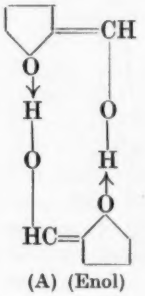
2-nitropropane has key bands at 11·7 μ and 8·8 μ, and 1-nitropropane at 8·1 μ; if nitromethane is absent 1-nitropropane can also be estimated on the 12·5-μ band.

A number of impurities was found in some of the samples, the chief ones being acetone, acetic acid, acetoxime, and 2 : 2-dinitropropane, and methods of estimating all of them were developed.

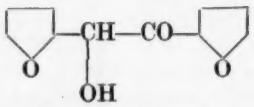
(4) *Investigation of the structure of tetrahydrofurfural dimer*

Freshly-distilled tetrahydrofurfural  is known to dimerize on standing, and the reaction is accompanied by changes in the infra-red spectrum, certain bands becoming weaker with time, while others, presumably due to the dimer, become stronger.

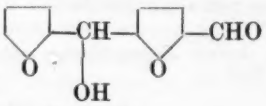
The possible formulæ for the dimer are :—



(A) (Enol)

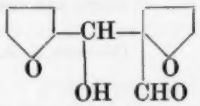


(B) (Benzoin)



(C) (Aldol)

and



(D) (Aldol)

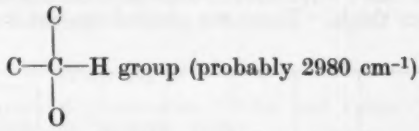
The infra-red spectra of the original material and the dimer were recorded

using both rock-salt and lithium fluoride prisms; the spectra show the following points :—

(i) The enol formula (A) is ruled out by the absence of bands at about 1640 cm^{-1} and 3200 cm^{-1}, wavelengths at which bands typical of carbon–carbon double bonds occur.

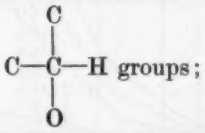
(ii) Bands at 1730 cm^{-1} (typical of the C=O group) and at 2710 cm^{-1} (typical of the C—H bond of the –CHO group) decrease in strength with time during the dimerization and extrapolation shows that the concentration of –CHO groups in the dimer is half that in the monomer. This shows that the dimer cannot have the benzoin formula (B); a dimer of this formula would have a band at 1730 cm^{-1} (due to the C=O) half as strong as the monomer, but would have no band at 2710 cm^{-1} (due to the C–H bond of the –CHO group). The behaviour of the 1730 and 2710 cm^{-1} bands is consistent with either of the two aldol formulæ (C) and (D), which are also supported by the increase in strength with time of a band at 3300 cm^{-1} which is due to a hydroxyl group.

(iii) The intensities of the bands due to the $-CH_2-$ group (1460 cm^{-1} 2890 cm^{-1} and 2925 cm^{-1}) and the

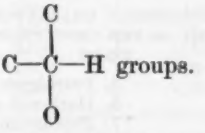


are difficult to measure accurately but no change with time could be observed.

If formula (C) is correct, dimerization will be accompanied by a slight decrease in the number of $-CH_2-$ groups and a doubling in the number of



if formula (D) is correct dimerization will be accompanied by no change in the concentrations of $-CH_2-$ or



The combined infra-red evidence thus favours the aldol formula (D), and this conclusion is further borne out by the chemical properties of the dimer.[13]

(5) *Evaluation of some petrolatums and petroleum jellies as sunburn preventives*

Interest has been aroused in the possible value of petrolatum and petroleum jellies as sunburn preventives.

It is known from previous work [14] that the erythemal (skin-reddening) effect of sunlight is almost entirely due to the presence of ultra-violet radiation. The wavelength of maximum erythemal effectiveness has been shown, both by experiment and from calculations based on the absorption properties of human skin and protein-type compounds, to be about 2975 Å. The ultra-violet and short-wave visible absorption and transmission characteristics of several grades of petrolatum and petroleum jelly were therefore determined.

The samples used were as shown below :—

	Clarification temperature, ° C
(1) White petrolatum	38–49
(2) Yellow petrolatum	44–46
(3) Amber petrolatum	45–48
(4) Dark-green petrolatum	59–61
(5) Petroleum jelly containing green dye	Sample too dark
(6) Dark-red veterinary petrolatum	53–57
(7) Petroleum jelly containing red dye	53–57

All the samples were examined in solution in mixed octanes, in the ultra-violet and visible region of the spectrum, and the results were used to calculate the equivalent transmission characteristics of liquid films 0·075 mm thick. These are plotted against wavelength in Fig. 8.

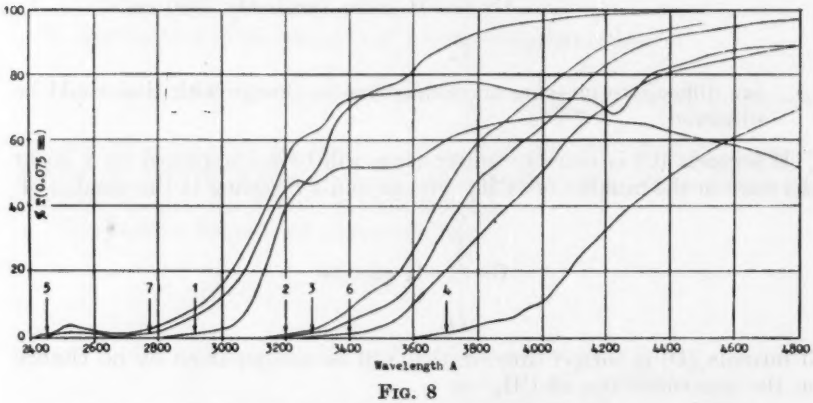


FIG. 8

ULTRA-VIOLET AND VISIBLE ABSORPTION CHARACTERISTICS OF PETROLATUMS AND PETROLEUM JELLIES, EXPRESSED AS PER CENT TRANSMISSION OF 0·075 MM LIQUID FILMS

1. White petrolatum.
2. Yellow petrolatum.
3. Amber petrolatum.
4. Dark-green petrolatum.
5. Petroleum jelly containing green dye.
6. Dark-red veterinary petrolatum.
7. Petroleum jelly containing red dye.

It will be seen that at the short-wavelength region of the spectrum all the samples have low transmission (high absorption), and for each the transmission increases as the wavelength increases. Consequently, for a given film thickness, the wavelength at which the transmission reaches a selected figure, in this case 1 per cent, can be used to compare the relative absorptions of the samples. These wavelengths are listed in Table II

together with the extinction coefficients at the wavelength of maximum erythemal effectiveness, 2975 Å.

TABLE II

Transmission Characteristics of Various Petrolatums

Sample no.	Description	λ * T1%	E (1% 1 cm) at 2975 Å
1	White petrolatum	2925 A	2·66
2	Yellow petrolatum	3200 A	10·7
3	Amber petrolatum	3275 A	12·1
4	Dark-green petrolatum	3675 A	24·9
5	Petroleum jelly containing green dye	2450 A	1·39
6	Red veterinary petrolatum	3400 A	19·9
7	Petroleum jelly containing red dye	2775 A (2475 A)	1·46

* Wavelength at which % T = 1%.

In addition to the measurements made in solution, samples 1 and 2 were also measured as solid films at room temperature, by filling 1 mm absorption cells with the molten sample and allowing this to solidify. Table III gives a comparison of the results obtained on both solid and " liquid " films.

TABLE III

Visible and Ultra-violet Transmission Characteristics of White and Yellow Petrolatum in Solid and " Liquid " States

Sample	Wavelength, Å	% T (1 mm) solid film	% T (1 mm) * " liquid " film
White petrolatum	6800	20·0	ca 100
	6000	18·4	ca 100
	5000	17·0	ca 100
	4500	15·2	95·0
	4000	10·0	66·1
	3500	1·0	2·0
	3000	<0·1	<0·1
	2500	<0·1	<0·1
Yellow petrolatum	6800	23·0	ca 100
	6000	21·2	ca 100
	5000	18·3	ca 100
	4500	11·9	53·0
	4000	0·8	2·2
	3500	<0·1	<0·1
	3000	<0·1	<0·1
	2500	<0·1	<0·1

* Values calculated for 100% vol/vol solutions, equivalent to undiluted samples.

It will be seen from Table II that the petrolatum samples 2, 3, 4, and 6 have extinction coefficients approximately ten times greater than samples 1, 5, and 7 at 2975 Å. Samples 5 and 7, which contain green and red dyes respectively, have additional absorption maxima at the longer wavelengths due to selective absorption by these coloured constituents. The results (Fig. 8) reveal too that in the ultra-violet the overall absorption of

the coloured petroleum jellies (Nos. 5 and 7) is even less than that of the white petrolatum (No. 1). The two dyed samples have apparently been prepared from highly-refined petroleum jellies so that their strong absorbing properties in the visible region are associated with relative transparency in the ultra-violet. On the basis of Fig. 8 and Table II, the samples can be placed in the following order of decreasing effectiveness as sunburn preventives :—

Most effective	Sample No. 4	Dark-green petrolatum
,, ,,	,, 6	Dark-red veterinary petrolatum
,, ,,	,, 3	Amber petrolatum
,, ,,	,, 2	Yellow petrolatum
,, ,,	,, 1	White petrolatum
,, ,,	,, 7	Red-dyed petroleum jelly
Least effective	,, 5	Green-dyed petroleum jelly

with the last three samples in a separate lower category than the other four.

This classification is confirmed for samples 1 and 2 by per cent transmission figures for 1 mm solid and " liquid " films (Table III) from which the apparently lower transmission of the solid films, due to additional light losses by scattering, can be estimated. For these two samples the differences between solid and " liquid " films are largest at long wavelengths, and are probably negligible below about 3500 Å. The clarification temperatures of the samples indicate that, with the possible exception of No. 1, they would probably exist as solid films at skin temperatures, under exposure to strong sunlight.

It is known that the ultra-violet absorption characteristics depend on the content of aromatic hydrocarbons and hence on the degree of refinement. Since the removal of aromatic constituents by solvent extraction, acid treatment, and earth contacting also progressively eliminates the coloured materials, the palest products have the lowest overall ultra-violet absorption. Furthermore, in the case of very highly refined petroleum jellies containing dyes added to give distinctive colours, intense absorption in the visible region will be associated with relative transparency in the ultra-violet. It is not possible to indicate the optimum degree of refinement for petrolatum to be used as a sunburn preventive, as less highly refined materials than, *e.g.*, dark-green or red veterinary petrolatums may contain skin-irritants, and clinical trials would be necessary to establish this point.

(6) *Continuous Examination of Plant Streams*

The applications of spectroscopy so far mentioned have involved the individual examination of a number of samples. It has long been realized that an instrument which could continuously examine a plant stream would be extremely useful. This is now possible owing to the successful outcome of one of the researches carried out under the sponsorship of the Hydrocarbon Research Group of the Institute of Petroleum, namely the development of an infra-red spectrometer in which the spectrum is made visible on a cathode-ray tube of long persistence. Instruments having this type of presentation have been constructed at both Cambridge and Oxford,[15-17] and their performance is such that it is possible to scan a range of approximately 3 μ in 12 sec anywhere in the region from 2 μ to 15 μ with an overall resolution sufficiently good for most work on complex molecules.

It was considered that this type of instrument would be an extremely useful tool for research and development work in the petroleum industry and that it would be practicable to develop such an instrument for use in an industrial laboratory. As there appeared to be no possibility of a commercial instrument of this type becoming available for some considerable time, one was constructed by co-operative effort. The basic circuit design was that of Daly and Sutherland.[17] The optics and scanning unit were constructed by the Research Department of the Anglo-Iranian Oil Co. Ltd. at Sunbury, and the electronics and " instrumentation " were by Messrs Marconi Instruments Ltd.

To exploit fully the advantages of such an instrument, it is essential that it may be easily moved into close proximity to any apparatus or plant on which it is to be used. This feature has been incorporated in the design of the instrument, which is built in the form of a single cabinet (Fig. 9) 6 ft long, 2 ft 2 in wide, and 3 ft 6 in high and mounted on four castors. It is of unit construction, and consists essentially of an optical system mounted on a box casting, a mechanically-operated scanning unit, an electronic amplifying system, and a cathode-ray display unit having a long-persistence screen and whose time base is synchronized with the scanning operation. A high-speed wax paper recorder is also included.

The optical system is built around the Hilger D88 monochromator, the detector being a Hilger Schwarz high-speed thermopile. The electronic system is a virtual copy of the Daly and Sutherland circuit,[17] and the scanning unit employs a gear-train system operated automatically through magnetic clutches. The estimated overall accuracy of the measurement of percentage transmission is about 2 per cent, the overall resolution being good enough for most work on hydrocarbon analytical problems.

The most important use which the instrument was expected to have was in connexion with problems in which the spectrum is changing, for example, the following of a distillation, chemical changes, changes of state, and other transitory phenomena, and it has been found that properly used on this type of work the instrument can save an enormous amount of time and trouble.

It has been used, for example, to monitor the overhead stream from a pilot-plant distillation. The distillate was circulated continuously through the absorption cell of the spectrometer, and the trace on the cathode-ray tube was compared with the spectrum of the desired product which had previously been drawn on a transparent screen placed over the tube. In this way it was possible to see exactly when the distillate had the required composition, and it was also possible to alter the column conditions to give the maximum product whilst ensuring that the quality was still satisfactory. Once these conditions were reached, changes in the spectrum displayed were taken to be due to slight changes in column conditions and it was possible to correct these very quickly. On one of these operations the instrument was in use for approximately 30 hours, and was sufficiently stable during this time to require no attention; and in fact for the major portion of the time the spectrometer was left in charge of the semi-skilled pilot-plant operator.

Another similar application, this time involving the following of a chemical change, was in connexion with investigations into the efficiency

of various catalysts for the desulphurization of petroleum products. For this work feedstocks consisting of solutions of thiophene in various petroleum fractions were used. After passing through the reactor, the effluent was continuously circulated through a variable-thickness absorption cell (a variable-thickness cell was used owing to the range of concentrations it was necessary to determine), and the thiophene content was instantaneously determined at any time by comparison with the spectra of a number of known solutions, making use of the thiophene absorption band near 14 μ. Figs. 10 and 11 show photographs of the traces obtained with solutions of thiophene in *iso*-octane and gas oil compared with traces of the solvents alone. In this way it was not only possible to get accurate time–sulphur content relationships, but it was immediately obvious when each run had achieved its object and the plant could be shut down without waste of time. In spite of the fact that the instrument was operating in the 13 μ to 15 μ range, it was sufficiently stable to allow the determination of thiophene with an accuracy of 0·01 per cent in the range 0 to 0·5 per cent. This work has enabled a short cycle test to be developed much more quickly than would have been possible by using a conventional type of spectrometer working on a series of spot samples. If spectroscopic equipment had not been available at all, the time involved in the analyses of the necessary samples would probably have been so long as to make this whole programme of work impracticable.

There are many other advantages of a rapid-scan infra-red spectrometer, particularly if it is capable of operation up to 15 μ. It may be used as a rapid-scan instrument for the preliminary examination of a problem in order to decide whether or not a more extensive study, using a more conventional instrument, is worth while.

It also allows of a rapid comparison of two materials, and in this application it is extremely useful in assessing the purity of a sample by comparison with a previously established pure material. At present this is carried out by using two cells, one containing the standard and the other the sample, and interchanging them manually between traces on the cathode-ray tube, an operation which is not easy in the 3 seconds available between successive traces. However, this application was envisaged when the design of the instrument was considered, and provision was made in the specification for a rapid cell-change system such that for the first trace one cell would be in the path of the beam, while for the following trace the second cell would be moved into position, the cell change taking place automatically during the flyback period of the time base of the cathode-ray tube. The electrical wiring required for this procedure has already been incorporated in the instrument, but the mechanics have yet to be completed. When they are completed this method of comparison will also be available on a continuous basis provided the circulating-type absorption cell is used.

Acknowledgments

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APPENDIX

Supply of Standard Hydrocarbon Samples

Specimens of certain hydrocarbons of high and certified purity may be obtained from the Chemical Research Laboratory, Teddington. The hydrocarbons are supplied in Pyrex glass ampoules fitted with break-tip seals and a certificate of purity as established by a suitable technique (*e.g.*, by a freezing-point determination or by mass spectrometry) is issued with each sample. The gaseous hydrocarbons are sold in 500-ml ampoules with the gas under 1 atmosphere pressure. The liquid samples are supplied in capsules containing 5 ml of liquid sealed *in vacuo*.

The list of hydrocarbons available will be revised from time to time, and it is expected that some additions will be made to the collection. Details of the materials available at any time and additional information on cost, etc., can be obtained from : Director, Chemical Research Laboratory, Teddington, Middlesex, England.

List of Hydrocarbons available as at Sept. 1, 1950

Paraffins	*Naphthenes*	*Diolefins*
Methane	*cyclo*Pentane	Butadiene-1-3
Ethane		2-Methylbutadiene-1-3
Propane	*Mono-olefins*	
n-Butane	Ethylene	*Aromatics*
*iso*Butane	Propylene	Benzene
n-Pentane	Butene-1	Toluene
2 : 2-Dimethylpropane	2-Methylpropylene	*o*-Xylene
n-Hexane	*cis*Butene-2	*m*-Xylene
2-Methylpentane	*trans*Butene-2	*p*-Xylene
2 : 2-Dimethylbutane	2-Methylbutene-2	
2 : 3-Dimethylbutane	Hexene-1	

SOME CRITERIA FOR COMMERCIAL SPECTROMETERS

By J. G. Reynolds *

Absorption spectrometers are rapidly becoming accepted as reliable research and routine analytical tools, particularly so in the petroleum industry, and it is felt that the time is opportune, therefore, for industrial

* "Shell" Refining and Marketing Co. Ltd.

users of spectroscopic methods to present what they consider to be the criteria for both a research instrument and a routine analytical spectrometer.

It is not easy to divide the uses of spectrometers into well-defined sections. On the one hand, research workers require a very versatile instrument, whereas plant operators prefer instruments with robust construction, simple manipulation, low cost, and only limited application.

Manufacturers have endeavoured, to some extent, to satisfy both demands in the same instrument at a cost midway between the two. It is felt, however, in describing the criteria for ideal commercial instruments that two models, one at very reasonable cost for plant operation, and one at higher cost for research work, would have the greatest economical usefulness. The plant instrument envisaged is not a small instrument that can be inserted in a production line for continuous-control purposes, but is a spectrometer in all senses of the word, but without those additions which enable the research instrument to aid the development of new plant techniques. For continuous control purposes, where only one component is being measured, specialized infra-red apparatus can be built, *e.g.*, gas analysers, but this type will not be discussed in this paper.

When considering a plant instrument, one assumes that it will be used mainly to control processes, where the actual compounds are known and their concentrations have to be kept within specified limits. It is obvious, therefore, that a fairly simple robust instrument, capable of being operated by semi-skilled staff in a plant laboratory, is necessary. Providing only moderate versatility is required, the cost can be kept to a minimum. In the following sections an attempt has been made to enumerate those criteria which are considered necessary and desirable in a plant instrument. In a research instrument a much greater versatility is required, and, within limits, the cost is of secondary consideration. Hence the ratio of desirable to necessary criteria will increase. It is fairly well known that spectroscopic instruments have been installed to perform analyses where conventional chemical methods are non-existent, or, at least, difficult and costly. Under these circumstances the instruments have paid for themselves very rapidly.

Infra-red Criteria

Dealing with the hypothetical plant instrument first, its components can be taken in logical sequence :—

Source

A self-starting source is necessary, preferably water cooled and of unit construction so that it can be plugged in like a radio valve. Some means should also be provided for small alterations in source position to get maximum energy into the entrance slit and to compensate for any distortion of the source during use. Two current strengths are desirable, one for normal usage and one at minimum current for use during temporarily inactive periods. This would considerably lengthen the source life.

It is essential in single-beam instrumentation that the source should emit constant energy. This may be achieved in two ways :—

(1) The mains supply may be stabilized by a constant-voltage transformer in conjunction with a barretter circuit.

(2) The energy emitted by the source may be controlled by a photocell which automatically alters the voltage supply to the source within reasonable limits.

This second method, known as "monitoring," is more desirable on a recording instrument than on one used mainly at fixed wavelengths and it is questionable in the latter case whether the increased cost is justified. Choice of a source (*i.e.*, whether Globar or Nernst) is dictated to a certain extent by the wavelength regions most likely to be used, but the Globar needs less ancillary equipment than the Nernst. Maximum concentration of available energy on the entrance slit is of fundamental importance, and it is reasonable to expect that it becomes more difficult to achieve as the source becomes larger. The Globar is usually much larger than the Nernst. The Nernst filament, furthermore, is operated at *ca* 2000° C and emits more energy than the Globar filament in the lower wavelength region (2–10 μ), whereas the Globar, operated at *ca* 1200° C, emits relatively more energy in the wavelength region above 10 μ (1000 cm^{-1}). It should not be inferred that any change in the operating temperatures of the sources would interchange the energy emitted. Other types of sources have different characteristics, but it has not been possible to make a strict comparison of the robustness and reliability of these sources, and much is left to personal preference.

Cells

Sample cells must be considered in two sections. Gas cells should be capable of being filled from outside the instrument casing. A system of ball-and-socket glass joints in the feed lines adjacent to the actual cell would enable the cell to be swung out of the energy beam when liquid cells are being used as gas cells permanently *in situ* decrease the energy available. The obvious requirements for a liquid cell are that its capacity should be small and its length variable (0·01 to 1·0 mm) and accurately reproducible. An alternative is a battery of cells of increasing length in series which could be filled simultaneously and operated on a slide. The cell giving the optimum absorption could then be introduced easily into the energy beam. On the plant it would be desirable if the operator could introduce the sample into the radiation beam without removing or touching the cell. The possibility of running a sample through the cell and watching its absorption continuously on a cathode-ray oscillograph seems very attractive.

Slits

Fixed slits have been used successfully on emission instruments, but not to the author's knowledge on absorption instruments. They should be cheaper than a continuously variable-slit mechanism and must be more reproducible. In the author's experience a system for the entrance and exit slits incorporating four such slits would be sufficient. Spectrographists have found variable slits easier to maintain free from dust than fixed slits, but in absorption work dust in the slit would affect the blank and sample cells equally.

It has been suggested that fixed slits could be formed by the deposition

of metal films on a suitable base material (*e.g.*, rock salt, quartz, etc.). It would then be possible to seal the instrument to keep it dust-proof and vapour-tight.

Wavelength

A scale calibrated in wavelength (or wave-number if so required) is preferable to one in arbitrary units which require conversion. Reproducibility of wavelength settings is vital. This latter point will require zero " backlash " in the wavedrum, which must be attained, even at the expense of a robust construction. Turrent mechanisms are ideal for use by a plant operator, but the number of wavelengths available rapidly becomes exhausted when several multicomponent analyses are required. A wavelength drive is more flexible.

Resolution

The resolution of the plant instrument should be consistent with the economical cost. Many purchasers demand a greater resolution than they would normally require. In present-day instruments it might be said that variations in the size of the prism face have a greater effect on cost than any other single component. Two commercial instruments having prisms of the same aperture, however, need not necessarily have the same resolution, since the quality of the mirrors is also a contributory factor. Different prism materials give optimum resolution in different wavelength regions, lithium fluoride at *ca* 4·5 μ (2222 cm^{-1}), calcium fluoride at *ca* 8·0 μ (1250 cm^{-1}), rock salt at *ca* 14·0 μ (714 cm^{-1}). Rock salt gives good overall resolution in the 2–15 μ range, and is therefore usually chosen. It might be thought that relatively small interchangeable prisms of different materials might give better general resolution over the whole wavelength range than a large rock-salt prism. Although this might cost little more, interchange of prisms on a plant instrument might be troublesome. It is essential if prisms are to be interchanged that wavelength calibration should be readjusted easily, *i.e.*, by separate wavelength scales.

False Energy

False energy may be defined as that energy received by the detector which has not passed along the normal path of the dispersed energy. In accordance with the " blackbody " curve, the proportion of false energy to total energy, while negligible at shorter wavelengths, increases as the wavelength increases and becomes significant above 10 μ (1000 cm^{-1}), and hence requires correction. This correction is usually made by interposing into the energy beam some material such as a glass plate which transmits the shorter wavelength radiation and absorbs the longer wavelength radiation. The response of the receiver with the glass plate in position is a measure of the false energy and enables the recorder to be reset to a new " zero." Any subsequent measurement with the glass plate removed from the energy beam will then represent the contribution of the real energy only.

Most instruments suffer to a greater or lesser extent from false energy. The majority of this may be eliminated by good focusing. The remainder may be corrected for by the use of a filtering system. A plant instrument

used for quantitative analysis in the 9- to 15-μ region *must* have a system of this kind.

Detector

In considering the detector system for a plant instrument, the accent is on sensitivity rather than speed. Hence a thermocouple is probably the better detector. This does not imply that if speed is required a thermocouple could not be used, but any detector chosen for the plant instrument must effect a compromise between these two requirements. Robustness is again essential. With regard to amplification of the detector output, D.C. amplification is reasonable in cost but has been proved to suffer from drift. Some improvement has been made in this defect. A.C. amplification does not suffer from drift, but may be a little more costly than D.C. since a " chopped beam " is necessary. Most manufacturers seem to prefer A.C. amplification. Since the electronic section of the apparatus is more susceptible to breakdown than the other sections, it is suggested that a complete replacement amplifier be made available. In this way the continuous use of the plant instrument is largely ensured. A very useful addition to the amplification system would be provision for cathode-ray presentation.

Since most plant instruments require the measurements to be made in terms of optical density at fixed wavelengths, a null-point potentiometer is probably the simplest device. Without this adaption it is necessary to record the spectra over a small wavelength range and measure the percentage transmission on the record. This would, however, require the addition of a scanning motor and accessories, etc., with the consequent increase in cost and bulk. Measurement of percentage transmission using a null-point potentiometer is much easier than computing it from a recorder chart. Should the spectra be required over a small wavelength range it can be plotted manually, if somewhat laboriously, using data obtained on the null-point potentiometer. Up to now no mention has been made as to whether the instrument should be a single-beam or a double-beam or memory-type instrument. If the latter categories are adopted the absorption measured would be that of the sample only. Using a single-beam instrument it is necessary to measure first the absorption of the sample plus background and then deduct that of the background. The single-beam instrument is considerably cheaper, probably more robust, and is therefore recommended for plant work.

General requirements

Some of the suggestions made in the preceding sections imply the movement of the instrument from one part of the plant to another. This could be achieved only if the instrument, amplifier, etc., were in a compact unit amounted on some type of trolley. Internal thermostatting is desirable to eliminate changes in wavelength calibrations. A compensating mirror could be used as an alternative, but might be rather slow in adjusting itself. It is essential that the vital components of the instrument (prism, mirrors, etc.) should be protected at all times by an efficient drying agent which can be frequently renewed. Absorption due to atmosphere can be trouble-

some, especially at longer wavelengths, and the removal of CO_2 by suitable absorbents, at least partially, should be attempted.

Research apparatus

One assumes that in considering a research instrument the accent is rather more on performance and versatility than on initial cost. The refinements, which would make the cost of the plant instrument prohibitive for the work performed, can therefore be allowed. Although single-beam instruments are at present being produced for combined research and routine work, it is expected that double-beam or memory-type instruments when readily available will supersede the single-beam instruments for research and the development of methods. A short description of these latter types of spectrometers might be in order here.

Double-beam spectrometers can incorporate one of two designs, the double beam in " space " or the double beam in " time " arrangement. The double beam in " space " models split the emitted energy into two beams, one of which traverses the " blank " cell and the other the " sample " cell simultaneously. Both empty cells must be matched over the whole wavelength range. Each beam is dispersed by the prism and received by separate matched detecting elements. The ratio of the energy responses of the detectors represents the percentage transmission of the sample. This type of instrument eliminates the atmospheric absorption bands fairly effectively. The double beam in " time " model, however, employs a revolving chopping mirror which allows the beam to traverse the " blank " and " sample " cells consecutively. As above, the chopped beam is dispersed by the prism and then is received by a single detector. Only when there is a difference between the absorption of the blank and sample will an alternating current be produced in the receiver. When this occurs, a servo-mechanism interposes a compensating shutter in front of the blank cell, until no alternating current is produced, *i.e.*, the energy falling on the detector is the same for both beams. The movement of this shutter is recorded and measures the percentage transmission of the sample. This type of spectrometer again eliminates the atmospheric absorption bands fairly effectively.

A memory-type spectrometer is of normal single-beam design. The blank cell is placed in the energy beam, and the slit width is automatically controlled so as to maintain the output signal constant. The slit width as a function of wavelength is recorded electromagnetically on a wire similar to that used for recording music. The sample is then placed in the energy beam, generally in the same cell as used for the " blank," and whilst the " sample " signals are being fed into the amplifier, the wire record of the " blank " absorption is played back. This holds the reference level constant, and so spectra appear as a conventional record of the percentage transmission of the sample versus wavelength. Elimination of atmospheric absorption in this type of instrument is best carried out by evacuation of the monochromator.

Although it might be considered that the single-beam instrument has probably been developed to its fullest economical extent, the same cannot be said about double-beam and memory instruments. No commercial

memory-type spectrometer is yet on the market,* but a prototype is in use. One commercial double-beam model is available in England and one in America at the time of writing, but others are approaching the manufacturing stage in both countries. Opinion seems to favour the double beam in " time " design.

The components of the hypothetical research instrument will also be considered in logical sequence.

Source

In order to obtain the maximum benefit from the good points of both Globar and Nernst, an interchangeable source unit utilizing both types seems practical. Any method of utilizing the source energy to greater advantage would be helpful, and a method involving multi slits has been suggested by Golay [1] with this end in view. Whether this method would be practical for incorporation into a mass-produced instrument is not known, but development of this idea should be encouraged. Monitoring of the source chosen is desirable, although in the double-beam instrument monitoring is not strictly necessary. A carbon arc as an infra-red source has been suggested [2] using an operating temperature of 3800° C. This improves the resolution of the instrument considerably, but the stability of the arc is doubtful, and continuous adjustment and replacement of the electrodes is tedious.

Cells

The cells described for use in the plant instrument could be equally adaptable to the research instrument, but provision might also be made for special types of cells not needed in the plant instrument. One example of this type of cell is the reflecting cell for gases. In this cell the incident energy is made to pass, by means of mirrors, along a path considerably longer than the dimensions of the cell itself thus enabling gases with low absorption to be measured accurately without using long, bulky cells. Other examples include micro-cells, and cells for low-temperature research, and since this research may become increasingly important, space should be allowed in the instrument for the cells used in this type of work which, on account of their insulation, are of necessity rather bulkier than standard type cells.

Slits

In a double-beam or memory-type instrument, the slits could automatically open to compensate for the fall off in incident energy in accordance with the blackbody curve, as the scan proceeds to longer wavelengths.

The choice between double-beam and memory-type instruments is difficult. To quote Van Zandt Williams [3] " The energy memory method has the advantage for very accurate analytical work that the same sample cell may be used empty and filled in the respective runs and does not require the carefully matched cells of the double beam method. However, the energy method would require accurate reproduction of source energy, calibration etc. over the period of the two runs, and would seem more

* The latest information received shows that a memory-type instrument is now available commercially.

tedious if a variety of sample types and phases are involved." To the research worker who has been accustomed to laboriously replotting data obtained on a single-beam instrument the difference seems largely academic. Both instruments produce spectra which are ideal for both interpretation and quantitative measurement.

Wavelength

The same recommendations apply for the research instrument as to the plant instrument with at least three scanning speeds. Continuously variable scanning speeds are not necessarily advantageous, since they may not be reproducible. Speed suppression, which slows down the scan when absorption becomes specific, seems a very desirable feature, and makes the overall length of a run without loss of resolution much shorter than when a constant slow speed is maintained.

Resolution

For the research instrument the resolution should be the best obtainable. This could best be achieved by the use of a suitable grating spectrometer incorporating a prism pre-monochromator. Up to now gratings have been used only in spectrometers to the special order of the purchaser. It would appear, however, that the supply position with regard to gratings may become easier, and it is possible that they may be used in commercial instruments. At present it will be assumed that prisms are to be used as the dispersive media. Hence the best resolution should be achieved by interchangeability of prism material combined with the use of the largest prism face possible. The carbon dioxide doublet at *ca* 4·2 μ and the ammonia doublet at *ca* 10·5 μ should be easily resolved with a rock-salt prism.

False energy

False energy can be removed effectively from all spectrometers. The best way of achieving this is by means of a double monochromator, whilst more general methods of elimination or correction include the use of filters or echelette gratings.

Detector

A chopped-beam system with A.C. amplification precludes any zero drift, and hence should be included in a recording instrument. Speed and sensitivity are both required, but as these cannot be obtained to a maximum degree simultaneously, a compromise must be effected.

Ease of replacement of the detector, *e.g.*, in the form of a plug-in socket, would be an advantage, and the window of the detecting element should preferably be made of material transparent up to at least 25 μ (400 cm^{-1}).

Measurement

In the ideal instrument it should be possible, as required, to read optical density and percentage transmission directly on a dial, to record the percentage transmission on a recorder, or to follow changes in absorption on a cathode-ray oscillograph over a specified wavelength region. From experience it is felt that there is less chance of error in measurement or in

confusion due to superposition of spectra at various cell lengths if a 10-inch chart is used in preference to a smaller one. The recorder should be fast and sensitive.

General requirements

Although thermostatting is essential, mobility and compactness are of much less importance in a research instrument than in a plant instrument. Complete eradication of atmospheric bands is obtainable only by evacuating the entire optical path. This has been carried out in a proposed memory-type instrument. Theoretically the double-beam method should compensate for atmospheric absorption in both beams, but this had been found difficult in practice. However, suitable absorbing agents in the enclosed portion of the optical path render compensation effective and relatively inexpensive. Presentation of the spectral record in a manner which is suitable for publication without any replotting is a decided advantage. Various checks have to be carried out periodically on both plant and research spectrometers. Two of the most important are mentioned below.

Accuracy of wavelength calibration

This check can be made by selecting a narrow waveband filter, which can be easily interposed into the energy beam, and recording the optimum optical density at selected wavelengths on each side of the band. Any significant wavelength drift will cause the difference in the two optical densities to increase considerably.

Provision should be made for resetting the prism assembly to bring the optical densities at the selected wavelengths back to their original values. It has been assumed, of course, that all instruments will be thermostatted for this procedure.

Linearity of amplification

This can be checked by the provision of electronic apparatus producing a standard range of input to the amplifier similar to that produced by the detector.

Finally, from the infra-red point of view, certain criteria have not hitherto been mentioned, such as maximum reflectivity of mirror surface, rigid mountings to eliminate the necessity for refocusing, the linearity of amplification, precision, and stability, as it is felt that these are conditions which all manufacturers try to attain and in which they can exercise no personal preference.

Visible and ultra-violet criteria

Ultra-violet and visible spectrophotometers are rather easier to review, since initial spectrophotometric investigations were conducted mainly in these regions, and in recent years manufacturers have tended to produce instruments which are similar in design. These are manually operated spectrophotometers, and their simplicity, robustness, and relatively low cost make them very suitable for plant work as defined in the introduction.

Briefly, a *manually* operated ultra-violet spectrophotometer should have stable sources and appropriate photo-cells covering a wavelength region from 2000 Å to at least 10,000 Å. Measurement should be made in optical

density or percentage transmission, and the wavelength scale should read directly in Ångstrom units, or mμ. Thermostatting is essential.

A battery of cells of varying length in series which can be filled simultaneously is very desirable. Alternatively, good variable-length cells, suitable for both water and organic solvents, would be useful.

For research work few commercial recording ultra-violet spectrophotometers are readily available in England, but certain criteria may be laid down with regard to their performance.

Optical density or, at least, percentage transmission should be recorded directly and in conjunction with a linear wavelength scale. Duplicate records should be reproducible to at least 0·5 Å in the 3000 Å range. The instrument should have flexibility of recording speed and chart drive. The record should be suitable for photographic reproduction for use in reports and in building a file of the spectra of pure compounds

The resolving power should be the best possible. For special applications such as the measurement of absorption at low temperatures and the determination of vapour spectra the half-band widths should not exceed 1 Å. However, for these special applications a higher noise level could be tolerated. The instrument could contain a slit drive so as to maintain constant energy at all wavelengths and thus secure the maximum resolution obtainable at a fixed signal-to-noise ratio. The slit drive could also be used to maintain a preselected constant band width and automatically raise the amplification such that the energy response is maintained at a constant level. It should be possible to use various types of cells, including one of multiple thickness. A moderately large cell compartment is essential for many special projects. The cell compartment and the monochromator should be thermostatted. The instrument should have sufficient sensitivity for recording weak emission spectra such as those produced by fluorescence and phosphorescence, but whilst it may not be desirable to add these demands to the performance criteria demanded of a high-accuracy absorption spectrophotometer, it is felt that mention should be made. Samples which fluoresce should be located in the entrance beam, whilst samples which are liable to photochemical decomposition should be located in the exit beam. The exit-beam position is usually preferred, but much depends on the nature of the sample. The best system would be to place the sample between the two sections of a double monochromator when these effects would be reduced to a minimum.

Whilst the criteria mentioned earlier might seem difficult to fulfil, it is felt that the dire need for such an instrument in England will spur the manufacturers to satisfy the requirements.

Acknowledgment

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References

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Discussion

Dr H. W. Thompson : I am sure that you will all agree that the papers which have been presented to us at this Symposium provide an impressive background to this story of the use of spectroscopic methods. Most of what has been described involves absorption measurements in the near infra-red and ultra-violet, but to include all the other relevant topics might have made the whole discussion unwieldy.

The authors have properly emphasized three main aspects, namely instrumentation, analysis, and structural diagnosis, and it is obvious that the applications are not confined solely to problems involving hydrocarbons themselves, but extend in perhaps even greater measure to other chemicals derived from the hydrocarbons in one way or another.

As I listened to the speakers to-night, I had mixed feelings of excitement and nostalgia—excitement because the story of the infra-red is a sort of fairy tale come true, and nostalgia because one will never again have the enormous fun, which Sutherland and I with our colleagues had, of helping to unravel this particular mystery in the earlier stages. As you no doubt all know, it is little more than ten years ago that measurements of molecular spectra in the infra-red were a trial of the most exacting kind, often regarded by some as pointless, and the instrumental developments since those days have been phenomenal.

This may not be the time to philosophize and moralize on the position, but I feel bound to draw your attention to one striking point, namely this, that we have here a vivid example of the value of pursuing scientific research in an apparently abstruse field for its own sake, with little obvious immediate practical applicability. If it had not been for the fact that during the fifteen years before 1940 a few academic laboratories had explored spectroscopic theory and molecular dynamics using simple molecules, often of no practical interest, then the rapid technical developments which have since taken place might have been of much smaller immediate practical value.

It may interest you to know how, in fact, infra-red analysis first came into being. About 1930 it was clear from Aston's work with the mass spectrometer that the atomic weight of hydrogen determined with this instrument did not agree with that obtained by chemical methods. Soon afterwards, about 1933, one of the lines in the atomic spectrum of hydrogen was found to have a satellite, and deuterium was discovered. When this new isotope had been isolated in quantity, " exchange " reactions were investigated, and the problem arose of analysing methane and the deuterated methanes. There were several possibilities, but in view of what was known about the theory of molecular vibrations, the near infra-red vibrational spectrum was studied. The results at that time were not particularly convincing, but they pointed the way to a new routine tool. Thus it all happened in a quite unexpected way.

I think that the Institute of Petroleum, through its Hydrocarbon Research Group, can feel both proud and gratified at the part which it has played in Britain in stimulating this progress, both by financial support and general encouragement; and I would stress its wisdom in allowing the work to a large extent to go its own way as the experiments themselves dictated rather than by planning on a utilitarian basis.

I will comment only briefly on the papers which we have heard. As regards instrumentation, there is now both a need and chance for more routine and analytical control instruments using both infra-red and ultra-violet. I think that the full potentialities of the so-called gas analysers have not yet been properly realized, and in spite of some temporary shortcomings these should be improved. It may be that new filters will be useful here, either of the reflection or transmission type. It is rather surprising that more attention has not been given commercially to reflection-interference filters made from thin layers of certain dielectric materials such as silicon monoxide, which give selective wavelength reflection and may be used instead of mirrors in an optical path.

There is plenty of scope for improving display systems in which an infra-red or ultra-violet spectrum, or a key part of it, is presented on a fluorescent screen. Here it would be valuable, although it may be a pious hope, to have more rapid sensitive detectors for the infra-red range 5 to 25 μ, for which at present no photo-conductive cells are available like those of lead sulphide or telluride in the range 1 to 5 μ. Incidentally, it seems possible now that such photo-conductive cells which can be made highly sensitive to the visible range may prove more convenient as detectors for Raman recorders than the usual photomultipliers or photo-cells with amplifiers.

As regards laboratory spectrometers, it is not yet certain that double-beam instruments have reached an entirely satisfactory stage of development. There are obvious advantages to an arrangement whereby any particular single-beam spectrometer—ultra-violet or infra-red—can at will be converted into an effectively double-beam system. Attachments of this sort using the alternation of optical paths caused by a rotating or oscillating mirror certainly seem to have been found commercially feasible, but I think that another electro-mechanical method recently described by Halford and Savitsky may have some more attractive features, as well as real simplicity, depending as it does upon a series of mechanical commutators with comparatively simpler electronic equipment.

Another feature which may well come under consideration soon for many spectrometers is the use of small diffraction gratings instead of prisms as dispersing agents. The main advantage of a grating over a prism is the greater ease of obtaining higher resolving power, though there may be other merits too. Against these, it is necessary in the infra-red to use echellette gratings, any one of which is effective only over a small range of wavelengths, and a set of such gratings is needed to cover the whole spectral range. Also, a fore-prism or filter device is required to prevent the overlapping of spectral data. If the problem involved justifies higher resolution, however, these experimental inconveniences are small, provided that the grating are available. Undoubtedly some of the work discussed tonight could benefit by the use of higher resolution, and it is therefore a very important development that gratings of all kinds and sizes—both replicas and originals—may very shortly be available in this country at very low cost.

As regards the analytical methods, I should only add that fluorescence measurements may be worth further examination for some problems, especially where qualitative differentiation is required. A good deal of

fundamental survey work remains to be done here, however, before this method can be made quantitative. The correlation rules which have been discussed for structural determinations are sometimes strikingly fruitful, but I feel that it is important to realise that many of them are not infallible, and in general they should be used with caution. It is not yet by any means possible to evaluate a complex structure completely from the infra-red spectrum alone.

These various possible improvements which I have mentioned represent, after all, only embellishments of the existing themes. You may wish me to mention other developments, some of which may at present seem far from having practical consequences.

There are, for example, detailed studies of the fine structure associated with certain vibration bands of gases or vapours. Elucidation of these fine structures requires the highest possible resolving power obtainable with grating spectrometers, and the most sensitive detecting systems. Such work is limited to comparatively simple molecules, but it leads to a more thorough understanding of the molecular dynamics of vibration and rotation. In this way we can hope to determine more exactly the molecular energy levels which are a prerequisite for the calculation of thermodynamic properties such as specific heat, free energy, or entropy. One special problem involved here is the free or restricted rotation of groups such as the methyl group about carbon–carbon bonds. This has to be fully understood for the calculation of thermodynamic properties, but it is also obviously of considerable importance in relation to the flexibility of long molecular skeletons such as occur in polymers or in rubber.

Secondly, I may refer to the problem of the intensities of infra-red bands. Strictly speaking, Beer's Law is applicable only to monochromatic radiation, but quite apart from this the comparatively poor resolving power of prism spectrometers introduces other complications in the case of light molecules of gases or vapours. Moreover, even with the heavier molecules we should, in principle, measure the band intensities by the integrated band areas rather than by peak heights. Accordingly, a careful study of the whole question of absolute extinction coefficients of vibration bands in the infra-red is needed, and this has recently been begun in several laboratories. It has led to an examination of what is termed the pressure broadening of bands, and although this sounds perhaps a somewhat academic matter the results have already suggested significant ways of improving accuracy in the analysis of mixtures of simple hydrocarbon gases.

The third important newer development is the measurement of spectra at low temperatures, say that of liquid air. At the lower temperatures some bands sharpen and are narrower. The smaller band width may become valuable when close bands are to be resolved, thus aiding analysis. There are, however, other important consequences, and although it is yet too early to estimate the full value of this kind of work, the simplified technique which has already been developed will surely be valuable.

Finally, I ought to mention a quite different kind of investigation, namely the examination of spectra in the very far infra-red, up to and including the region of microwaves. This now remains about the only part of the known electromagnetic spectrum which has not been properly studied, and it will certainly involve a good many experimental problems.

On theoretical grounds it involves the regions in which the molecule absorbs rotational energy or low-frequency vibrations, and while it is unlikely that in general it will prove as useful for many purposes as the near infra-red has been, yet it is certain that it thould be properly explored and that important results will emerge from it. Indeed, it seems already that we have to consider the possibility of using microwave absorption for certain analytical procedures, since it is possible here to obtain with comparative ease an extremely high degree of resolution, and lines corresponding to different molecules can be separated. Before the full value of this can be proved, however, we must know more about the spectra of more substances, and in this respect we are only yet at the beginning.

I think that I have said enough not only to emphasize the value of the work which has been described by the earlier speakers but also perhaps to suggest that there are still important fields of this kind to be explored.

Dr W. L. Hyde: May I first introduce myself? Until September 1950 I was a physicist in the Research Department of Baird Associates, in Cambridge, Massachusetts, U.S.A., who make the infra-red spectrometer and other scientific instruments. I am now a Scientific Liaison Officer at the American Embassy, in the Office of Naval Research.

My present job, scientific liaison, is part of a broad programme for the support of fundamental scientific research which has been in operation under the American Navy ever since the end of the war. The military research sponsored by the Navy is done by other branches, leaving the Office of Naval Research free to concern itself solely with basic science. In a similar manner our military liaison with the British is conducted almost entirely by men in uniform, leaving us who represent O.N.R. free to concentrate on basic science. In this activity we feel with some pride that we are representatives of the entire American scientific effort as well as of our Navy.

Scientific liaison ought to and does work both ways. The members of our staff are eager to learn about interesting developments which the British are engaged in, and we are also eager to help in every way to make the results of research in the U.S. available to you. Our office in Grosvenor Square is full to overflowing with progress reports and reprints on research now in progress in the United States, and I hope that those of you who are not familiar with our activities will not hesitate to get in touch with me.

In the United States there are now two infra-red spectrometers which have had extensive and varied use; in addition, there are several that have been produced in smaller quantities or on an experimental basis. The most important of these is a simple single-beam instrument. This instrument gets the major credit for the wide use of infra-red spectroscopy in our industrial laboratories and schools. It is still the instrument of choice for most infra-red spectroscopy. One should not start with the most expensive and elaborate equipment. This instrument is carefully built to very close tolerances, so that its resolving power approaches the theoretical limit. It is available as a monochromator alone or with a wide choice of accessories. That is the most fundamental way in which to approach this complex field of instrumentation.

The second instrument commonly used is a double-beam spectrometer.

It has found its widest and most important application in laboratories primarily concerned with organic analysis; the pharmaceutical chemists and the petroleum chemists in particular have made valuable use of it.

These two instruments characterize the trend that is occurring as infra-red spectroscopy comes out of the laboratories of the physical chemist and theoretician into the organic laboratories. This development has been slow, partly because those who have been most familiar with infra-red spectroscopy in the last twenty years have under-estimated the value of the technique. That is to say, it has been a source of amazement to all of us in infra-red spectroscopy to learn how far it is possible to go in organic analysis by the empirical study of organic spectra. The theoretician has been over-eager to point out the fallacy of attributing bands in an infra-red spectrum to the functional groups of the molecule. The organic chemist has either ignored the theoretical complexity of the problem or has been unaware of it and has been able to make remarkable progress by pure insight.

This application of insight is difficult enough, but it is essentially impossible when the experimental results are meagre or are available in an awkward form. Thus, infra-red spectroscopy has turned out to be most valuable in those laboratories where the spectra were available easily, rapidly, and on a uniform basis of chart size, resolution, and spectral range. Dr Powell has shown that, in order to elucidate the last step in the understanding of the thymol dimer, it was necessary to compare with thirty-one collected spectra. This idea that you have to have a wide selection of spectra on a uniform basis easily available is the development which I believe characterizes the work in the United States most significantly; and it is my most important message tonight.

During the last five years several industrial laboratories in the United States began to attack this problem very vigorously. They have collected libraries of 10,000 to 20,000 infra-red spectra and have catalogued these in most elegant ways, using punched-card techniques and elaborate cross indexing. In the last two years it has become apparent that this step is so valuable that it is desirable to transfer the activity to some central authority and thus avoid the tremendous duplication that was taking place. A Committee has been organized under the direction of Dr Carl Creitz at the National Bureau of Standards to collect and prepare infra-red spectral information in a uniform manner from the laboratories now compiling these curves, and to distribute it to those who need it. This is not an easy thing to do. The same complexity which gives unique value to an infra-red spectrum also makes it impossible to characterize it in any simple manner. To a certain extent the important effort being made by the American Institute of Petroleum to do this for a large series of compounds has resulted in spectra which are rather cumbersome, inconsistent, and awkward to use. The Creitz Committee has chosen to put these infra-red spectra and many others on punched cards, punched to indicate the constituents of the molecule, the wavelengths of the principal absorption bands, and a wealth of other information. Printed on each card is a picture of the spectrum, the name of the compound, and references concerning its preparation and the source of the spectrum. A library of such cards makes it possible to segregate spectra characterizing a certain class of organic

compounds, or to attack the analysis of an unknown with little or no knowledge other than its spectrum. The idea in this activity is, of course, not to do an analysis entirely by infra-red spectroscopy, but to make the maximum possible use of it in conjunction with other chemical methods.

Mr Reynolds has described to us the two types of instrument which he feels would best serve industrial infra-red spectroscopy, one being a very complex instrument for research, and one a very simple instrument primarily for urgent plant use. I would suggest that the trend I have described might lead to a need for three instruments. First, there is the universal and versatile research instrument which, so to speak, will do everything. Frankly, I am a little dubious that there is a legitimate demand for such an instrument. A new American instrument, using the memory system, is a remarkable example of such a universal instrument. The second instrument, and the one which I think will be most important, will be one primarily for organic analysis. It should be rapid and reproducible, but should have only medium resolving power; *i.e.*, a high signal-to-noise ratio and rapid performance are much more important than high resolution. It should present its spectra on charts of a uniform size and scale, preferably with some attention to the standards now being fixed. It should spare no expense to ensure reliable operation, but should be pretty severely stripped of accessories and gadgets.

After these two instruments have come into wide use, I think there will develop a market for a particularly simple single-beam instrument of very low resolving power, one which will compete with the gas analyser in certain complex compounds which may be beyond the capacity of the simple gas analysers. This is my own idea and is not commonly shared by manufacturers, either in Britain or abroad. I think that, as infra-red techniques grow more common for quality control and process control, there will develop a market justifying an instrument of exceeding simplicity and that it should be possible to make this instrument exceedingly cheaply. I am afraid, however, that such a development would be premature at this time.

I want to reinforce the remarks of Dr Thompson on the importance of the gas analysers, for I feel that they have been neglected. The developments in the United States have lagged behind those in Britain, and I am much impressed by what I have seen here.

Dr A. E. Martin (Messrs Sir Howard Grubb, Parsons & Co.): As the representative of one of the two manufacturers of gas analysers in Britain, I think I can put the minds of Dr Thompson and of Dr Hyde at rest by assuring them that we have not been neglecting gas analysers by any means. However, it has taken four years to learn how to make them, but I think that from now on progress will be very rapid.

I have already replied to Dr Reynolds in detail concerning the design of the ideal spectrometer, and I do not propose to say much more about it just now. But there is the point that, I think, only three firms in Britain are interested in infra-red spectrometers, and that probably means that about twenty people are actually thinking about these instruments and their design. Obviously, it is not possible to cover the whole field, including single-beam and double-beam instruments, the utilization of the reflection microscope and polarized light, low-temperature work and other

matters. For ourselves, we are mainly trying to make a good single-beam spectrometer and a good double-beam instrument derived from the single-beam. Obviously, if you have a spectrometer with high resolution, you can always convert it into a low-resolution instrument. Making a new instrument of low resolution is, we feel, at this stage an undesirable diversion of effort.

With regard to the accurate measurement of the transmission of a sample at spot wavelengths, the recorder normally used can be replaced by a meter graduated 0 to 100. Stray light can be allowed for very easily by off-setting the meter zero so that zero on the meter is given when a piece of glass is interposed in the beam, full scale being given for the blank, of course.

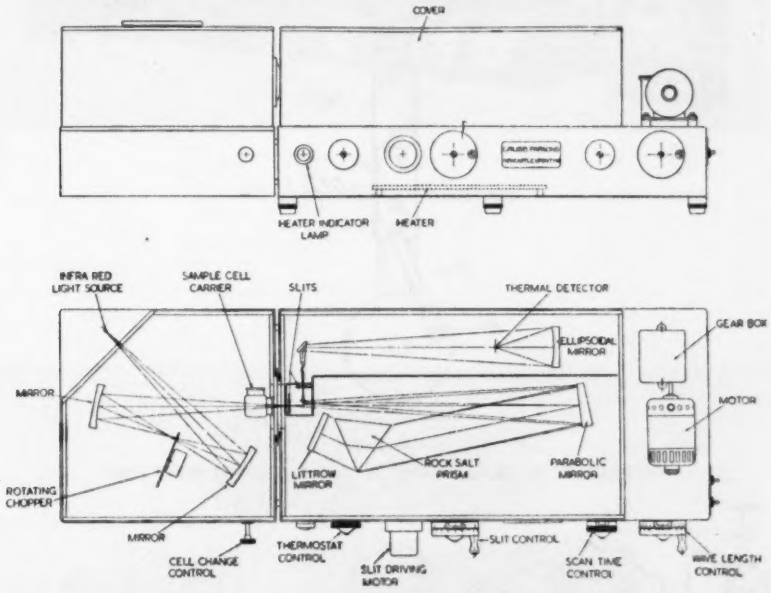


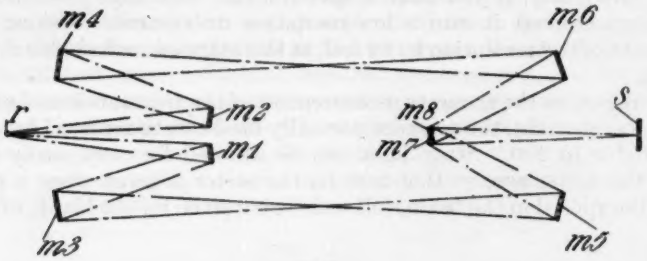
FIG. 1

THE OPTICAL ARRANGEMENT OF THE GRUBB PARSONS SINGLE-BEAM SPECTROMETER

When the sample is put in the optical path, the transmission, corrected for stray light, can be read off directly. If you want to go farther you can graduate the scale in optical densities, so that the optical density, corrected for stray light, is read off directly. The scale will not be linear, of course; full scale will correspond to a density of 0, half scale to 0·3, and quarter scale to 0·6. I have a rather deep-rooted dislike for non-linear scales; but no doubt if the user wants a meter graduated in this way the manufacturers, Messrs Sangamo-Weston Ltd., will be happy to supply one.

Fig. 1 shows the optical system of the Grubb Parsons standard single-beam spectrometer. The radiation unit, shown on the left, was designed rather hurriedly, the chief requirement being compactness. It was not expected that every user would be satisfied with it, but in fact it has generally been accepted and only quite recently has Dr Powell asked for

something rather more elaborate and flexible. Fig. 2 shows the standard single-beam equipment set up ready for use.



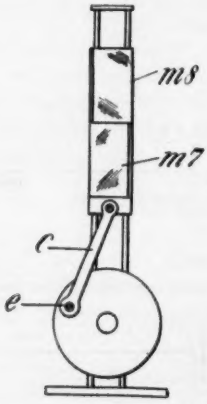


FIG. 3

DIAGRAM OF OPTICAL SYSTEM OF DOUBLE CONVERSION UNIT

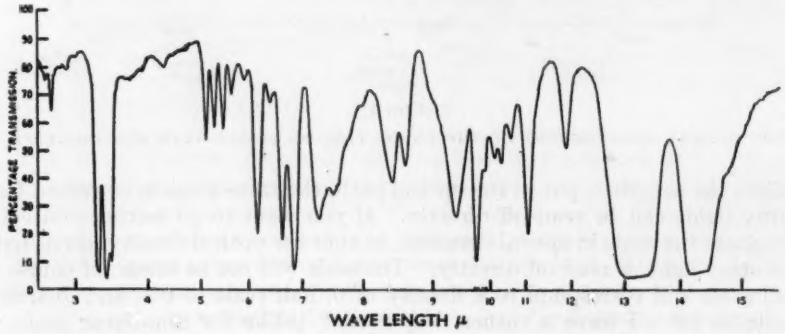


FIG. 5

THE ABSORPTION SPECTRUM OF POLYSTYRENE FOIL A FEW THOUSANDTHS OF AN INCH THICK

Fig. 3 shows diagrammatically the optical system of the double-beam conversion unit; it is very simple and effective. This unit simply replaces the normal radiation unit and attaches directly to the spectrometer. The complete instrument is shown in Fig. 4, the spectrometer being to the right

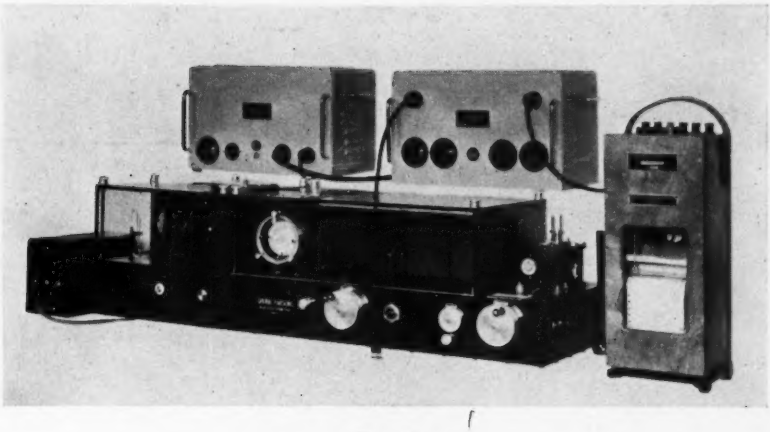


FIG. 2

S.3 INFRA-RED SPECTROMETER

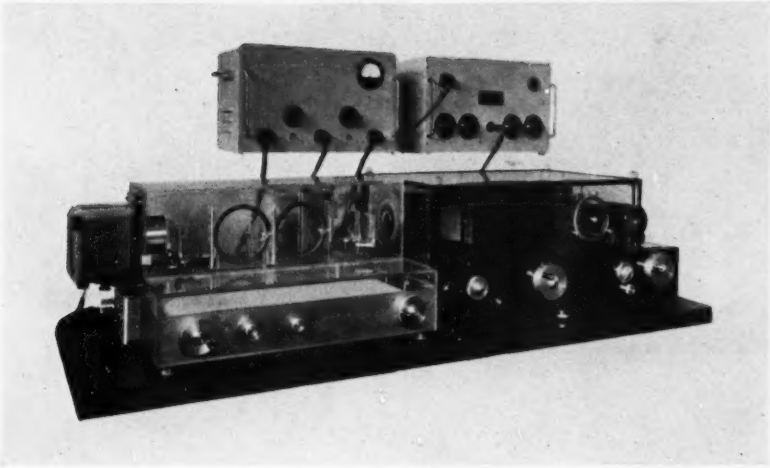


FIG. 4

DOUBLE-BEAM INFRA-RED SPECTROMETER

[*To face p.* 142.

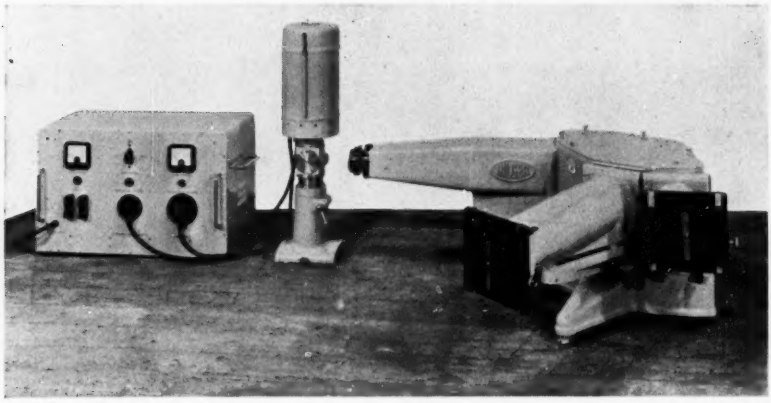


FIG. 6

A RAMAN SPECTROGRAPH

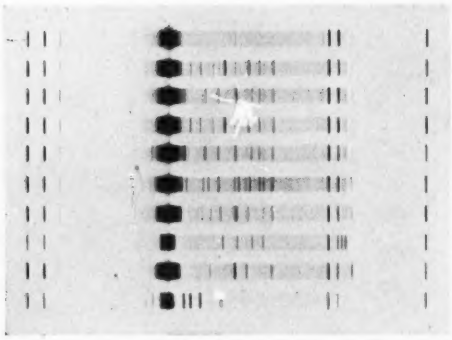


FIG. 7

Raman spectra of :

1. Mercury (light source only)
2. Mixture ortho- and para-xylene
3. Mixture ortho-, meta-, para-xylene, and ethyl benzene
4. Para-xylene
5. Meta-xylene
6. Ortho-xylene
7. Ethyl benzene
8. *cyclo*Hexane
9. Benzene
10. Carbon tetrachloride

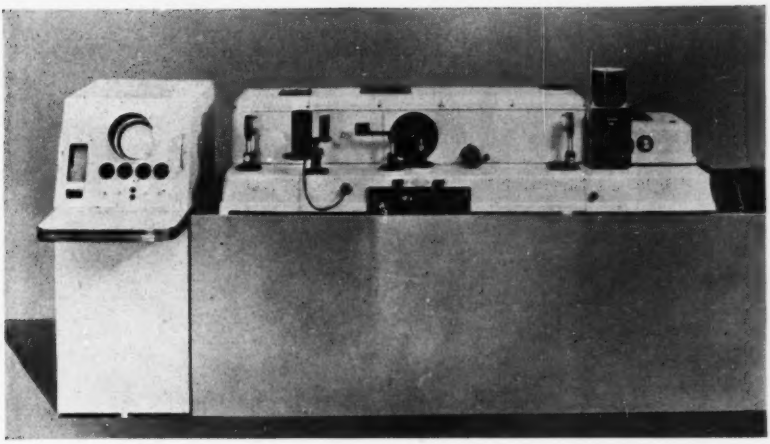


FIG. 9

INFRA-RED SPECTROMETER WITH CATHODE RAY DISPLAY

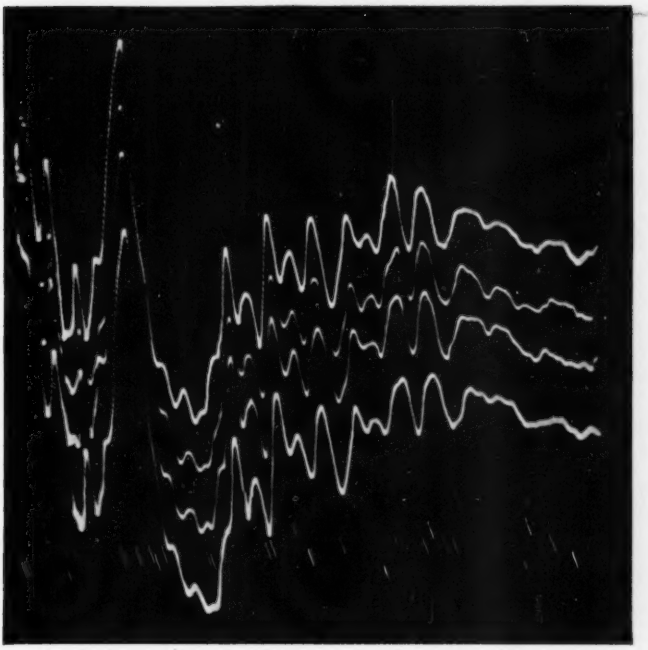


FIG. 10

6 μ WATER VAPOUR BANDS PHOTOGRAPHED FROM CATHODE RAY SCREEN

and the Nernst housing on extreme left. The amplifier is only slightly modified from that used in the single-beam instrument, while the recorder, which is simply a motor-driven pen, is built into the instrument. Difficulties such as pen friction, slow speed of response, etc., are eliminated, and there is an important advantage in that we can make the recorder ourselves and build it into the spectrometer instead of depending on recorder manufacturers.

An example of a spectrum recorded with our double-beam spectrometer is shown in Fig. 5. The spectrum from 2 to 15 μ can be run off in as short a time as 10 minutes. By running more slowly the resolution can be increased somewhat.

Dr A. C. Menzies (Messrs Hilger & Watts Ltd.): We have heard from Dr Sheppard about Raman and infra-red spectra and the complementary nature of the information obtained from each.

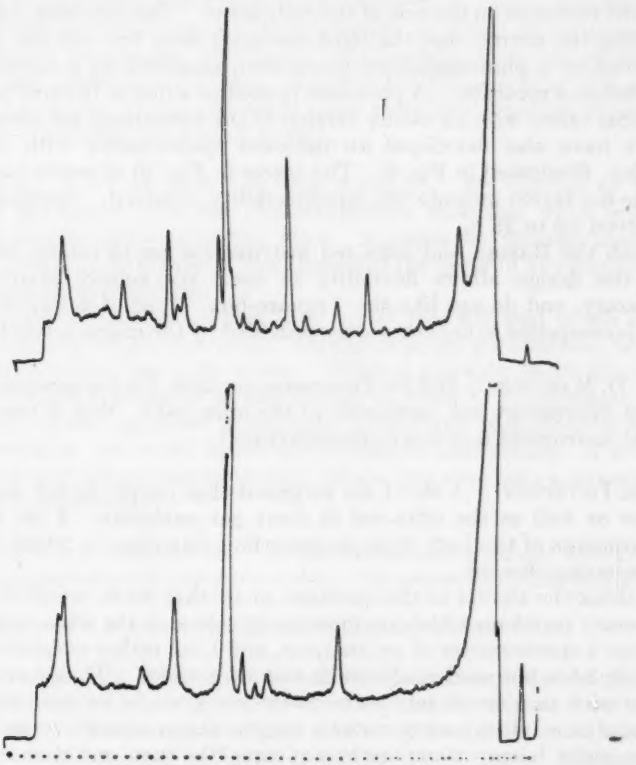


Fig. 8

RAMAN SPECTRA OF BENZENE AND TOLUENE

The demonstration by the lecture bench is of a scanning Raman spectrograph. This is our first model and it consists of a scanning attachment to the photographic instrument shown in Fig. 6. A control unit supplies

power to four mercury lamps surrounding the specimen, which is contained in a vertical glass tube with a plane window at the bottom. The lamps are surrounded by a water-jacket coated inside with magnesium oxide, and the specimen tube is contained in two concentric glass tubes providing space for a filtering liquid and a coolant. The spectrograph has two large prisms each with refracting angle a little over 60°. The two cameras are provided, one of short focal length and aperture F/1·5 with which very strong Raman lines have been photographed in $\frac{1}{10}$ sec, and one of longer focal length and aperture F/5·7 with which the spectra in Fig. 7 were taken in 1 min. The two cameras are on a rotatable mount and can be interchanged without loss of alignment by turning the mount.

The two cameras are on a rotatable mount and can be interchanged without loss of alignment by turning the mount.

For scanning purposes, the short-focus camera is replaced by a plane mirror which directs the light back through the dispersing system to an exit slit mounted on the side of the collimator. The spectrum is scanned by rotating the mirror, and the light emerging from the exit slit is chopped, received by a photomultiplier (uncooled), amplified by a tuned amplifier, and fed to a recorder. A photocell is used to monitor the source intensity. Records taken with an earlier version of the instrument are seen in Fig. 8.

We have also developed an infra-red spectrometer with cathode-ray display, illustrated in Fig. 9. The traces in Fig. 10 of water-vapour bands in the 6-μ region indicate the reproducibility obtained. Spectra have been observed up to 23 μ.

Both the Raman and infra-red instruments are of robust construction, but the design allows flexibility in use. We believe this to be very necessary, and do not like the " square-box " type of design in which the user is compelled to use accessories provided by the manufacturer concerned.

A. D. Makower : Did Dr Thompson say that, for gas analysis, the ultra-violet instrument was preferable to the infra-red ? Was it that the ultra-violet instrument cost less to manufacture ?

Dr Thompson : I said I am surprised that people do not use the ultra-violet as well as the infra-red in these gas analysers. I am referring to instruments of the Luft type, or something like that, in which there is not a dispersing element.

I think the answer to the question, in another sense, would be that there are many problems which are more easily solved in the ultra-violet, whether we use a spectrometer or an analyser, and I am rather surprised that more people have not used analysers in the ultra-violet. Things are sometimes done with an ultra-violet spectrometer which might be done as easily with an analyser. It is easy to make a burglar alarm across a room by using an ultra-violet beam ; there are lots of cases like that, and that is the point I was trying to make.

G. C. Eltenton : I was impressed by the beauty of the fine-structure spectrum of methane shown by Prof. Thompson, and by his comments on the gas analyser. In the early days of optimism about this type of apparatus one tended to regard it as an instrument of high resolving power,

since the detector gas was a kind of " infinite resolving power grating," to use a loose expression. However, in practical applications to the monitoring of hydrocarbon streams, lack of discrimination is more serious than lack of sensitivity. To overcome this defect it would appear to be necessary to sacrifice the sensitivity inherent in pressure broadening, and to work at low pressures in both the sample and the detector. This should increase the discrimination, if, and only if, other hydrocarbons (in which one is usually more interested) possess a structure sufficiently fine for differentiation to occur within two overlapping absorption bands. Does Prof. Thompson consider that hope lies along these lines? Does not the comparative absence of pressure broadening in the higher hydrocarbons indicate that however far we try and push the resolution, the fine structure will remain relatively undeveloped?

DR THOMPSON: Mr Eltenton's comments involve several rather complicated considerations, and I cannot deal with them here. Whether one sees rotational fine structure in a band depends, of course, in some measure upon pressure broadening, but more significantly upon the molecular geometry and moments of inertia. I am not quite sure that the points which he has raised at present really bear upon the question of the gas analyser, if I understand them correctly.

DR HYDE: A lot of work has been going on. Dr Billings at Baird Associates has made both the Denison-Hedley reflection filter and the Turner Frustrated total reflection filter. A paper by Billings described the latter filter, and he obtained band passes of the order of five-hundredths of a micron in some instances.

But there is no immediate threat that any of this will lead to the evolution of a genuinely simple instrument analogous to the gas analyser, because the complication becomes quite severe. While I was with Baird Associates I started a counter-offensive on this matter in order to demonstrate that, if one made similar sacrifices in resolving power and complication in the prism instrument, one could finish with a simpler instrument; if you say you demand only 10μ resolution as with filters, you can make a remarkably simple prism instrument.

DR THOMPSON: I agree with your remarks about a simple instrument. One firm has made one for the ultra-violet. However, the point is arguable.

THE CHAIRMAN: I have considerable sympathy for the filter.

DR REYNOLDS: Dr Thompson feels that the memory standardization type of instrument is a white elephant. This may be so, but it certainly works. I was working in a laboratory where a prototype was in use, and one girl kept two of us busy interpreting the spectra obtained. Admittedly, electronic troubles were encountered, though not to the extent suggested. Breaking of the recorder wire, though infrequent, was irritating, but could be reduced to a minimum by supervision.

DR THOMPSON: As regards the memory recorder spectrometer, I think in the first place, that it costs 26,000 dollars. Certainly you can achieve

extremely elegant results with it; I have been to California and have seen it myself. But the accuracy you can achieve with it is surely no greater than you can achieve by simpler and cheaper methods. I do not wish to be offensive, but I think that you can do just as well much more cheaply, and I am all for cheapness and simplicity.

THE CHAIRMAN: I have three rather pleasant duties. First, I want to express the appreciation of the Institute and of all of us to the instrument manufacturers and to all who have gone to enormous trouble to show us their equipment here and to illustrate it by slides, and for having taken part in the discussion. We do appreciate their help very much; we have put them to much trouble during the last six years—and we shall go on doing it for the next six years!

Secondly, I have to express to all speakers this evening our thanks for their willingness to tell us what they have been doing, how they have done it, why they have been doing it, and why they want us to go on helping them. We have not often the chance to get all these people together here; it has been a great pleasure to have been able to do that tonight. Altogether it has been a very edifying experience.

Finally, I wish to place on record our appreciation and thanks to the sponsoring companies for their continued support of this work.

The Chairman's expressions of thanks were warmly applauded, and the meeting closed.

ACID TREATMENT OF SHALE GASOLINE. PART I. HYDROLYSIS OF THE ACID SLUDGE

By R. C. Mathews and G. E. Mapstone *

Summary

The quantity of acid extracted by hydrolysis of the acid sludge is independent of the proportion of water used. The total tar content (soluble and insoluble tars in the hydrolysed acid) was found to decrease with increasing acid concentrations above 6*N*. Also the specific gravity of both the hydrolysed acid and the insoluble tar increased with increasing acid strength.

The hydrolysed acid precipitated tars spontaneously. The freshly precipitated tars were found to be soluble in a number of solvents. On standing for a few weeks these tars decomposed with the evolution of foul-smelling gases, and were then found to be only sparingly soluble in the solvents, leaving a gritty residue.

The hydrolysed acid appreciably corroded mild steel pipe at temperatures above 200° F. A maximum rate of corrosion being obtained with approximately 7*N* acid. Sulphuric acid inhibited with tar bases condensed with benzaldehyde showed corrosion rates at 200° F comparable with hydrolysed acid. Sulphuric acid inhibited with tar bases showed a higher rate of corrosion and did not exhibit the maximum value with acid concentration.

Introduction

The treatment of raw gasoline with concentrated sulphuric acid is normally carried out for the removal of unstable gum-forming constituents (such as conjugated diolefins) and organic sulphur compounds. During this treatment a significant proportion of the olefins present in the gasoline is polymerized and, because of their high boiling point, the treated gasoline must be redistilled for the removal of these polymers. The problems associated with the acid treatment of gasoline therefore involve not only the actual treatment process but also the disposal or utilization of the spent acid sludge and the redistillation of the gasoline and disposal of the re-run bottoms.

Previous Work

The description of the acid-treatment process as operated at Glen Davis has been presented elsewhere.[1]

The acid sludge is readily hydrolysed with water to give a tar and dilute sulphuric acid, a reaction which has been used to aid in its disposal. The tar, which has been used as fuel oil, has been shown [2] to consist of neutral oils and tars containing some sulphur and nitrogen and a small amount of tar acids with traces of sulphonic acids. The dilute or "hydrolysed" acid which is used for the treatment of the crude shale oil emulsions [1, 3] contains higher pyridine homologues equivalent to approximately 10 per cent of the sludge, some pyrroles and sulphonic acids, and a trace of alcohols.[2]

The hydrolysis of the sludge on the plant has been carried out by running it into water until the aqueous layer of "hydrolysed" acid was 10–11*N* with free sulphuric acid. Although the hydrolysis is carried out in an unlined mild steel tank, corrosion by the acid has not been significant over

* National Oil Pty. Ltd., Glen Davis, N.S.W.

a period of about five years, most of the relatively slight corrosion being in the upper section of the tank in contact with the hydrolysed tar.

Operating Troubles

The hydrolysed acid is used for the treatment of crude shale oil emulsions,[3, 4] and normal practice has been to store it in a mild steel tank until required and to pump it to a small intermediate storage tank at the treatment plant as required. On standing, the hydrolysed acid deposits a heavy tar which caused trouble by blocking the pipeline. The use of high-pressure steam has been necessary to clear these blockages, partly by the effect of the temperature in softening the tar, and partly by the pressure. After approximately two years' service the pipe failed in several places by corrosion. The following work was therefore carried out in order to determine the optimum conditions for the hydrolysis of the acid sludge and for handling the hydrolysed acid.

Experimental

Hydrolysis of the Acid Sludge

The hydrolysis of the acid sludge was examined at a number of concentrations varying from 80 per cent sludge, 20 per cent water, to 20 per cent sludge and 80 per cent water. Measured volumes of the sludge and water were mixed in a separating funnel, and the hydrolysed acid separated from the insoluble tar after settling for 2 hours. Their respective volumes and specific gravities were measured and the normality of the acid determined by titration with 0·2*N*-caustic soda to phenol phthalein end-point.

On standing for three weeks, approximately 2 and 4 per cent of tar precipitated from the 2·5*N* and 14·1*N* hydrolysed acid respectively. After this time of standing, the soluble oils, which included a large percentage of tar bases, were determined by neutralizing the acids with equivalent quantities of 5·5*N*-caustic soda solution. The results shown in Table I are corrected to include the tars precipitated on standing.

Table I

Acid Sludge Hydrolysis

Vol sludge, ml	Vol water, ml	Sp. gr. of tar at 60° F	Vol acid, ml	Acid normality	Sp. gr. of acid at 60° F	Vol. sol. oils,* ml	Sol oils †	Tar †
100	0	1·475	—	14·8	—	—	—	—
80	20	1·042	88	14·1	1·324	41·0	51·2	15
70	30	1·031	86	12·3	1·295	33·8	48·2	20
60	40	1·023	86	10·5	1·259	29·6	49·4	23
50	50	1·003	84	8·2	1·214	25·4	51·6	36
40	60	0·989	86	6·4	1·165	18·2	45·6	37
30	70	0·982	87	3·7	1·104	12·0	40·0	43
20	80	0·978	90	2·5	1·070	6·8	34·0	50

* Corrected for tars precipitated on standing. This figure includes the tar bases present. † As per cent by volume of the acid sludge.

Properties of the Spontaneously Precipitated Tar

When fresh, the spontaneously precipitated tars from the hydrolysed acid were completely soluble in ethyl alcohol, concentrated sulphuric acid,

carbon disulphide, cresylic acid, and the recycle light oil from the Dubbs cracking plant. These tars were readily oxidized to give a brittle mass on exposure to air. An oxidised tar sample obtained from the acid storage tank was partially soluble in concentrated sulphuric acid, carbon disulphide, and benzol, and sparingly soluble in ethyl alcohol. The insoluble residue was a hard, gritty mass.

The freshly precipitated tars evolved pungent-smelling gases continuously for several weeks on standing at room temperature.

Determination of Corrosion Rate

The rate of corrosion of mild steel by the hydrolysed acid was determined by using ½-inch lengths of 1-inch pipe. The pipe specimens were steam cleaned and then smoothed with fine emery paper before measuring to determine the surface area. A weighed piece of the pipe was placed in a 250-ml beaker and covered with 150 ml acid maintained at the required temperature by standing at :—

(*a*) room temperature (70°–80° F);
(*b*) 100° F in a water-bath;
(*c*) 200° F in an oven;
(*d*) their respective boiling points.

The specimen remained in the acid for a time sufficient to give a measurable weight loss without pitting, this time having been determined by experiment. It was then washed under running water, any corrosion scale removed mechanically, and adherent tars removed by washing with alcohol, before drying at 200° F for 2 hours and weighing.

Tar Bases

The tar bases used in this work were isolated from the hydrolysed acid by neutralization with caustic soda solution. The crude bases were dried over solid caustic soda and distilled.

The condensed tar bases were prepared by refluxing the tar bases with 10 per cent by volume of benzaldehyde for 2½ hours over anhydrous zinc chloride.[5] The zinc chloride was separated by filtration through glass wool.

Corrosion tests were carried out on 3*N*-, 6·13*N*-, 9·29*N*-, and 12·4*N*-sulphuric acid with additions of tar bases and condensed tar bases varying from 0 to 20 per cent by volume of the mixture. The free acid and total acid content of each solution was determined by titrating with sodium hydroxide to screened methyl orange and phenolphthalein end-points respectively.

The condensed tar bases were not completely soluble in the sulphuric acid, but, since filtered solutions deposited some tar on standing at 200° F, the remainder of the samples were not filtered. This tar gradually changed into a black brittle substance on standing for two days.

The oily precipitate recovered from the solution of the condensed bases in acid was added to another sample of 6·13*N*-sulphuric acid and the rate of corrosion determined. Some of the oil, equivalent to 0·35 per cent of the bases by volume, dissolved in the acid during the test at 200° F.

All corrosion tests with the tar bases were carried out at 200° F only. The time of contact of the metal specimen was varied with the rate of

corrosion. When free acid and tar bases were used, the time of contact varied between ½ and 4 hours, as the rate of attack was rapid and a layer of ferrous sulphate soon formed on the pipe. However, with the condensed tar bases the rate of attack was slow, and a time of contact of 18 to 24 hours was required to measure the corrosion rate. In this case a varnish-like film deposited on the metal was cleaned off with methylated spirits prior to weighing.

Discussion

Hydrolysis of Sludge

From Fig 1 it is seen that the percentage of insoluble tar decreased linearly with increasing concentration of the hydrolysed acid and that the percentage of soluble tars increased, but approached a constant value in the

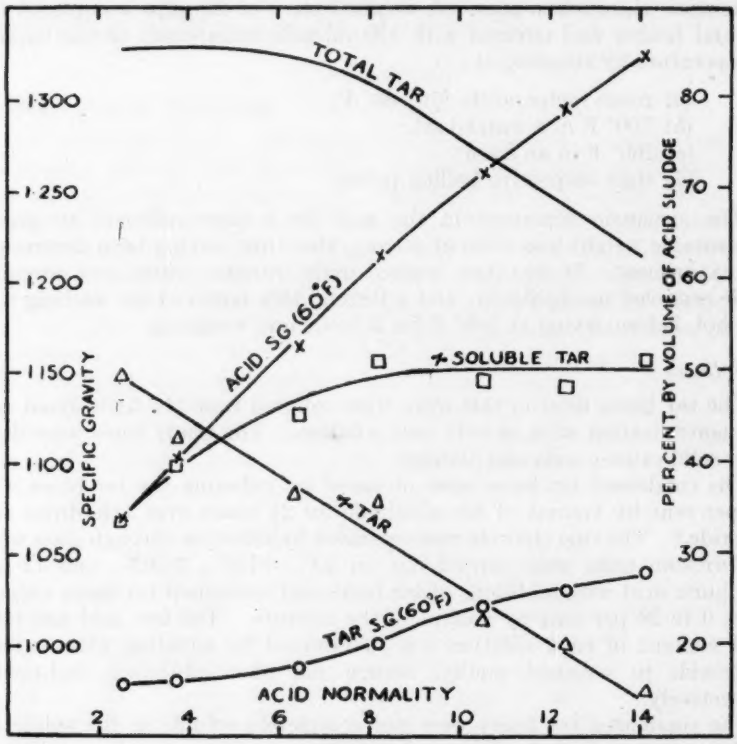


Fig. 1

PROPERTIES OF HYDROLYSIS PRODUCTS AT VARIOUS NORMALITIES OF HYDROLYSED ACID

8·5*N* and stronger acid. Therefore, instead of being constant for all acid strengths as was expected, the total tar content was constant only up to 6*N* acid and, in the stronger acid, decreased linearly with increasing acid concentration. If it was a question of only relative solubilities in the varying strength acids, the per cent insoluble tars would also approach a con-

stant value in the 8·5*N* acid. However, this was not the case, and it appears as though there was some type of decomposition of the soluble oils at concentrations higher than 8·5*N* acid, the nature of which is unknown. This was borne out to some extent by the specific-gravity curves shown in Fig. 1. As the specific gravity of the acid increased with increasing acid strength, which is the normal relationship, it would be expected that the specific gravity of the tar would decrease; however, they both increased. The tar also became increasingly viscous. This meant that the less viscous and lower-specific-gravity constituents of the tar were more soluble in the stronger acid. It is interesting to note that the approach to the constant value of soluble oils and the point of inflexion in the specific-gravity curve for the tar were in the vicinity of the acid strength which had the maximum rate of attack on mild steel.

Corrosion by Hydrolysed Acid

The rate of attack of the hydrolysed acid on the mild pipe increased with temperature and was dependent on acid strength, approaching a maximum

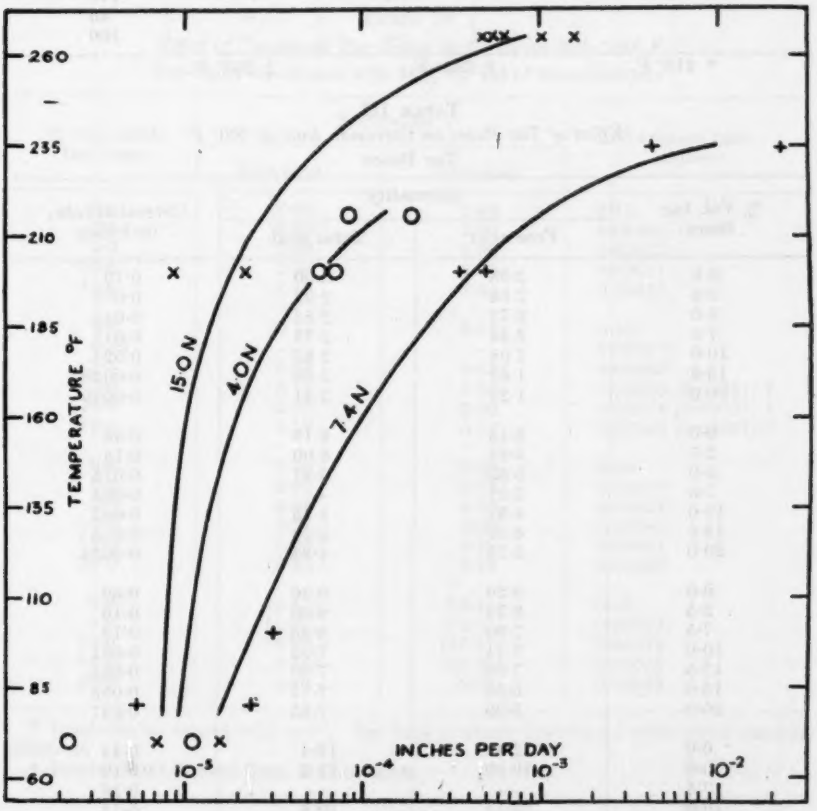


FIG. 2

EFFECT OF TEMPERATURE ON THE CORROSION RATE OF HYDROLYSED ACID

TABLE II

Rate of Corrosion of Mild Steel Pipe by Hydrolysed Acid

Expressed as inches/day 10^{-3}.

Temperature, ° F	Acid strength		
	4*N*	7·4*N*	15*N*
70	0·22	—	1·7
	1·04	—	0·71
80	—	2·4	—
	—	0·54	—
100	—	3·0	—
200	6·0	50	0·83
	7·3	34	2·1
Boiling point of acid . . .	8·9 *	410 †	160 †
	18	2300	44
	8·2	—	58
	8·2	—	170
	—	—	46
	—	—	100

* 216° F. † 234° F. ‡ 265° F.

TABLE III

Effect of Tar Bases on Corrosion Rate at 200° F

Tar Bases

% Vol. tar bases	Normality		Corrosion rate, inch/day
	Free acid	Total acid	
0·0	2·98	3·00	0·19
2·5	2·84	2·92	0·076
5·0	2·72	2·82	0·045
7·5	2·34	2·78	0·011
10·0	2·08	2·65	0·021
15·0	1·61	2·50	0·0036
20·0	1·21	2·41	0·0019
0·0	6·13	6·13	0·48
2·5	5·81	6·00	0·15
5·0	5·55	5·81	0·075
7·5	5·21	—	0·065
10·0	4·92	5·75	0·042
15·0	4·32	5·20	0·013
20·0	3·73	4·94	0·0054
0·0	9·20	9·20	0·50
2·5	8·72	8·90	0·16
7·5	7·90	8·35	0·14
10·0	7·21	7·96	0·061
12·5	7·05	7·80	0·084
15·0	6·59	7·72	0·058
20·0	5·99	7·25	0·037
0·0	12·40	12·4	0·44
5·0	10·90	11·3	0·19
7·5	—	—	0·16
10·0	10·15	10·8	0·13
15·0	9·32	10·3	0·051
20·0	8·35	9·6	0·041

value in the region of 7*N* acid (Fig. 2 and Table II). The acid strength was of considerable importance in the higher ranges of temperature; for example at 215° F the corrosion rate of the 15*N* acid ($3{\cdot}0 \times 10^{-5}$ inch per day) was only one-fortieth of that of the 7·4*N* acid ($120 + 10^{-5}$ inch per day). At temperatures below 115° F the corrosion rate was negligible, being of the order 3×10^{-6} inch per day and was not seriously influenced by the acid concentration.

It is appreciated that, under the conditions of the tests, diffusion effects would have a significant effect on the observed corrosion rates. However, since these factors are also significant under the plant conditions, it was felt that the technique adopted should give results comparable with those experienced on the plant.

Corrosion Inhibition by Tar Bases

Since the tar bases present in the hydrolysed acid were known to be active corrosion inhibitors, the rate of corrosion of mild steel pipe in sul-

TABLE IV

Effect of Condensed Tar Bases on Corrosive Rate 200° *F*

Tar bases condensed with 10% by vol of benzaldehyde

% vol. cond. tar bases	Normality		Corrosion rate, in/day
	Free acid	Total acid	
0·0	2·98	3·00	0·19
2·5	2·88	3·00	0·00048
5·0	2·69	2·90	0·00013
10·0	2·36	2·83	0·00011
15·0	2·16	2·84	0·00015
0·0	6·13	6·13	0·48
0·35	—	—	0·0015 *
2·5	5·45	5·65	0·00035
5·0	5·15	5·55	0·00028 (0·00061) †
10·0	4·32	5·30	0·00074 (0·00057) †
15·0	4·18	5·25	0·00042 (0·00037) †
0·0	9·20	9·20	0·50
2·5	8·60	8·75	0·00030
5·0	8·28	8·70	0·00027
10·0	7·74	8·30	0·00080
15·0	6·95	8·10	0·00062
20·0	6·45	7·75	0·00063
0·0	12·4	12·4	0·44
5·0	11·0	(11·3)	0·00033
10·0	10·20	(10·8)	0·00013
15·0	9·30	(10·3)	0·00012
20·0	8·40	(9·6)	0·00023

* Insoluble oil mixed with acid. Tar base content determined after metal sample removed.

† Insoluble oil filtered from acid solution.

phuric acid containing the purified bases was examined. The results showed that the tar bases did inhibit corrosion (Table IV, Figs. 3 and 4).

However, the corrosion rates were fifty to a hundred times greater than those with the hydrolysed acid.

The experimental relationships shown in Fig. 3 can be written:

$$0{\cdot}32 \log C = F/A - 1{\cdot}12 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C = corrosion rate at 200° F in inches per day;
F = Free acid normality (to screened methyl orange);
A = Initial acid normality prior to the addition of the tar bases.

The tar bases contain approximately 10 per cent of nitrogen by weight and a mean specific gravity of 0·93. If the small changes of volume on

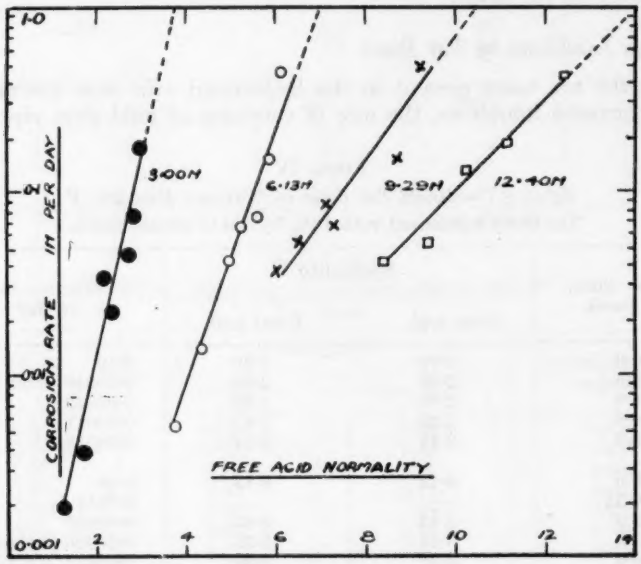


FIG. 3

RELATION BETWEEN FREE ACID NORMALITY AND CORROSION RATE OF SULPHURIC ACID CONTAINING ADDED TAR BASES

mixing the tar bases and acid are neglected, equation (1) can be rewritten in the form

$$\log C = 0{\cdot}47\, F\, [(6{\cdot}65 \times F)/T - 1] - 3{\cdot}5 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where T is the total sulphuric acid normality. The total and free acid contents are easily determined, and this equation may be used to estimate the rate of corrosion of mild steel pipe at 200° F by sulphuric acid inhibited with the distilled shale tar bases.

Corrosion Inhibition by the Condensed Tar Bases

Since styryl pyridines could be expected to be stronger corrosion inhibitors than the parent bases, the shale tar bases were condensed with benzaldehyde. The reactive α- and γ- methyl (or methylene) groups con-

dense with the aldehyde to form 2-hydroxy-2-phenyl-ethyl groups. Subsequent dehydration forms the styryl group. Since the filtered acid solutions of the condensed bases gradually deposited some tar, it would appear that this dehydration reaction continued to take place slowly in the acid solution.

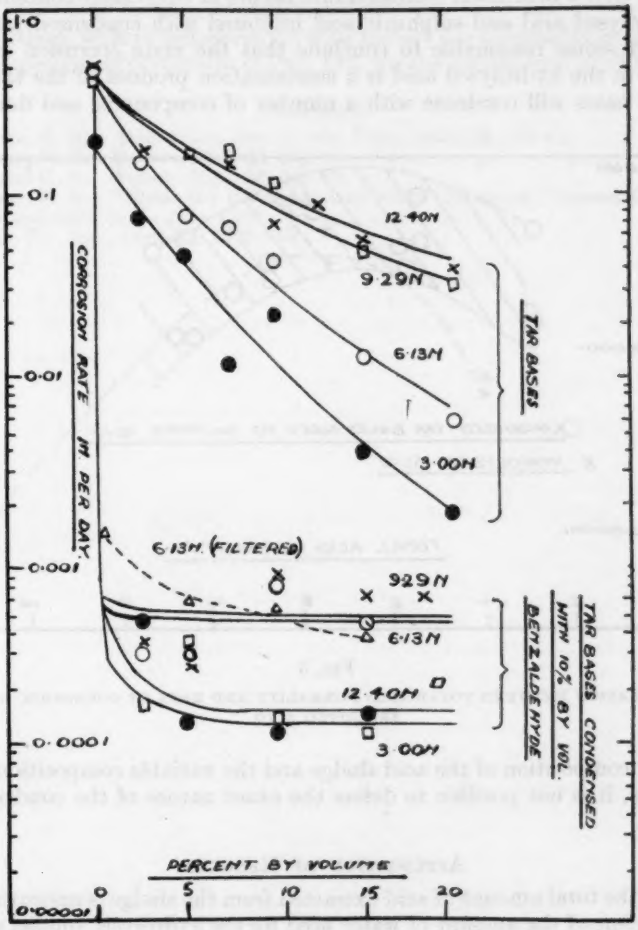


FIG. 4

EFFECT OF VOLUME OF TAR BASES ON THE CORROSION RATE

The condensed bases showed an entirely different corrosion-inhibiting effect to that exhibited by the distilled bases. In this case the rate of corrosion was independent of the amount of condensed tar bases present and appeared to be a function of the initial concentration of the sulphuric acid, as shown by Fig. 4. It may be expected that the decrease in total acid concentration brought about by the dilution on the addition of the tar

bases would effect the corrosion rate. However, there is no such trend shown by the curves in Fig. 4 or in Fig. 5 when the total acid content is plotted against corrosion rate.

The rate of corrosion by the hydrolysed acid at 200° F has also been plotted in Fig. 5. There is a definite trend shown by the points which indicate that a maximum corrosion rate occurs at equivalent concentrations of hydrolysed acid and sulphuric acid inhibited with condensed tar bases. Hence it seems reasonable to conclude that the main corrosion inhibitor present in the hydrolysed acid is a condensation product of the tar bases. The tar bases will condense with a number of compounds, and due to the

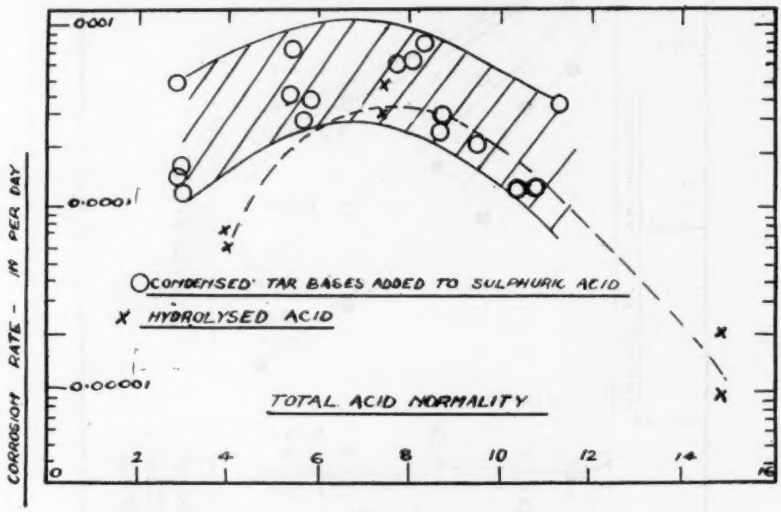


FIG. 5

RELATION BETWEEN TOTAL ACID NORMALITY AND RATE OF CORROSION BY INHIBITED ACID

complex composition of the acid sludge and the variable composition of the tar bases, it is not possible to define the exact nature of the condensation product.

APPLICATION OF RESULTS

Since the total amount of acid extracted from the sludge is approximately independent of the amount of water used for the hydrolysis, smaller storage facilities are required by keeping the hydrolysed acid as concentrated as practicable. Because of the dark colour of the hydrolysed acid, plant experience has indicated that this should be in the range of 10 to 11*N* maximum in order to obtain a visible separation between the tar and acid.

The corrosion results indicate satisfactory life for the storage tank and lines as long as the temperature is kept low. The corrosion experienced in the pipelines appears to have been due to the high temperatures caused by steam purging the lines to remove tar accumulations. Since these accumulations were formed by the tars precipitated on standing, they would be

reduced by pumping the acid to storage as soon as possible after hydrolysis. Because of the spontaneous decomposition of the precipitated tar and its ready oxidation to give insoluble products, solvent cleaning of the pipeline appears to be impracticable.

Acknowledgment

The authors wish to acknowledge with thanks the permission granted by the management of National Oil Pty. Ltd. for the publication of this paper.

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THE UNIT OF HEAT

THE Royal Society has recently circulated to its Fellows and to scientific societies, a memorandum under the title "The Unit of Heat." This is reproduced below, and comments on the applicability of its recommendations to the petroleum industry will be welcomed. Such comments should be sent to the General Secretary of the Institute of Petroleum.

The Council of the Royal Society, after careful consideration of the following memorandum entitled "The Unit of Heat" and consultation with the Society's Sectional Committees, recommended that in the Society's publications quantities of heat, and all other dependent concepts such as specific heat, latent heat, heat of combustion, entropy, etc., should in future be expressed both in joules and in calories.

After the receipt of this communication Fellows of the Society are therefore asked to adopt this practice, and to see that it is followed by authors of papers communicated by them to be considered for publication in *Proceedings* or *Philosophical Transactions*. To facilitate this, tables of conversion factors are appended below, together with examples of its use in textual, tabular, and diagrammatic matter.

The Council of the Royal Society also agreed to circulate to other scientific societies a statement of the action which they were taking in regard to units of heat.

E. J. SALISBURY
D. BRUNT
} *Secretaries, R.S.*

CONVERSION FACTORS FOR VARIOUS CALORIES

Description of calorie	Value in joules	Reciproal of value in joules
International steam cable calorie (I.T. cal.)	4·1868	0·23885
15° calorie (cal. $_{15°}$)	4·1855	0·23892
4° calorie (cal. $_{4°}$)	4·2045	0·23784
Thermochemical calorie or defined calorie	4·1840	0·23901
Mean 0° to 100° C calorie	4·1897	0·23868

CONVERSION FACTORS FOR VARIOUS BRITISH THERMAL UNITS

Description of unit	Value in joules	Reciprocal of value in joules
60·5° F British thermal unit	1054·54	0·00094828
Mean 32° to 212° F British thermal unit	1055·79	0·00094716
39° F British thermal unit	1059·52	0·00094383
Steam table British thermal unit (1939)	1055·06	0·00094781

EXAMPLES

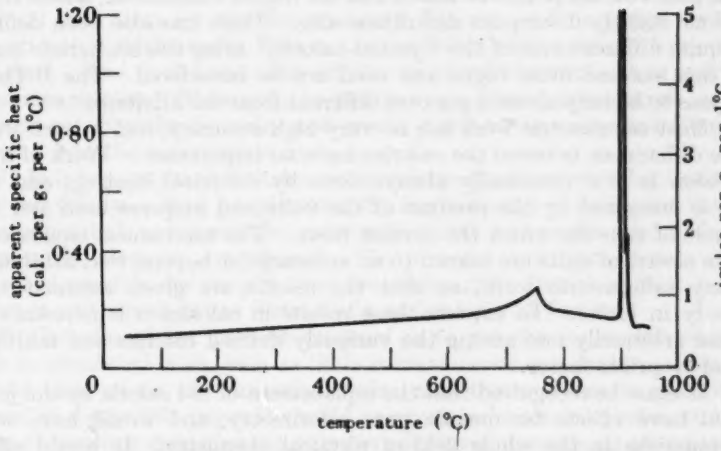
1. *Textual*

Heat of combustion of carbon monoxide in oxygen is 67·56 k.cal.$_{15°}$ per mol (282·8 k.J. per mol).

2. *Tabular*

Author	Date	Heat of formation of N_2O (k.cal. per mol)	(k.J. per mol)
Berthelot	1880	−20·6	−86·2
Thomsen	1882	−17·7	−74·1
Sutton	1932	−20·5	−85·8
Fenning and Cotton	1933	−19·74	−82·6
Awbery and Griffiths	1933	−19·5	−81·6

3. *Graphical*



MEMORANDUM ON THE UNIT OF HEAT

By Sir Charles Darwin, F.R.S. (*Chairman of the Symbols Committee of the Royal Society*)

1. It has recently been agreed by all the important international bodies concerned that the joule, of 10^7 ergs, is to be the *basic* unit of heat. This is a decided matter, and there can be no doubt of the correctness of the decision. The reasons are briefly as follows.

The First Law of Thermodynamics states that heat is energy, and it is therefore proper that it should be measured in the same units as energy, that is the joule. Hitherto the unit has been the calorie, which was chosen rather arbitrarily more than a century ago for its practical convenience, because the early work in calorimetry was mostly done by observing the change of temperature of a water-bath. Thus the calorie involved the idea of temperature which is quite irrelevant to the First Law, and it also had reference to an arbitrarily chosen specific substance, water. To use the calorie it was thus necessary to have a number, the mechanical equivalent of heat, which masqueraded as a universal physical constant, though in fact it is nothing but the specific heat of water measured in energy units.

2. The next point is that there are quite a number of different calories in use, differing perceptibly in magnitude, and so making a lot of confusion. The most usual is perhaps (1) the 15° calorie (from 14½° to 15½°), and very nearly but not quite equal to (2) the International Steam Table calorie. Then there is (3) the 4° calorie (which has the advantage of giving the specific heat at constant volume, since it is at the point of maximum density of water), (4) the Thermochemical or "Defined" calorie, and (5) the Mean calorie (from 0° to 100°). The differences between these range over one part in two hundred. There has also in the past been a minor source of confusion because some writers used the term calorie for the "Great Calorie" (of a kilogramme instead of a gramme); this should be, and now usually is, called the kilocalorie.

There is a very similar state of confusion over the British Thermal Unit, based on the pound of water, and the degree Fahrenheit, where there are four slightly discrepant definitions also. There has also been defined the quite different unit of the " pound-calorie," using the centigrade scale, but this has had little vogue and need not be considered. The B.Th.U. happens to be only about 5 per cent different from the kilojoule.

3. Most calorimetric work has no very high accuracy, and in such work these differences between the calories have no importance. Work of high precision is now practically always done by electrical heating, and the heat is measured by the product of the volts and amperes used and the seconds of time for which the current flows. The mechanical equivalents of the electrical units are known to an accuracy far beyond that attainable in any calorimetric work, so that the results are given automatically directly in joules. To express these results in calories it is necessary to choose arbitrarily one among the variously defined calories and multiply the appropriate factor.

4. It must be recognized that the replacement of the calorie by the joule would have effects far outside pure calorimetry, and would have wide repercussions in the whole field of physical chemistry. It would affect not only specific heat, latent heat, and heat of combustion, but also entropy, internal energy, enthalpy, free energy, Gibbs function, and thermal conductivity. It may be noticed that for some of these the work is often not calorimetric; for instance, many free energies are determined by the voltage of an electrolytic cell, so that here again the determination would be more naturally done directly in joules.

5. The fact that the joule is the basic unit does not necessarily imply that it has got to be used in actual practice, but it would be the natural thing to do, and as has been said, there are a good many cases where it is the quantity actually determined by experiment. The theoretical advantages are overwhelmingly in its favour but the contrary arguments must also be considered. The only really strong argument against it is that it is always inconvenient to make any change of units. Nearly all work in the past has been expressed in calories, and the numerical values, if now given in joules, will be unfamiliar to most people. The process would have the same sort of inconvenience as that of converting British units of mass and length into metric, but it would be far less troublesome, because there is only a single multiplying factor, instead of complicated products of various powers of mass and length, which are needed for the various mechanical quantities. However, this point cannot be invoked as an argument in favour of the joule, since we are forced to convert from British to metric system in order to be comprehensible to foreigners, whereas the calorie is as much used abroad as at home.

6. If the line is taken that the change to the practical use of the joule is too inconvenient to be considered, there is still to be faced the variety among the different calories. In the present instructions given by the International Unions of Physics and Chemistry it is laid down that, where values are given in calories, the conversion factor to joules is always to be stated. This makes a formally self-consistent system, but it is certainly not convenient. A better solution on these lines might be to select a particular value, and define the calorie as, say, exactly 4·187 joules. A

difficulty about such a proposal is that it would have to be agreed first by the leading workers (some of whom have vested interests in particular values) and then by the International Unions, and to judge by past experience it might easily take ten years before such agreement would be reached. And in the end after all this we should be left with a unit that was meaningless. Moreover, as pointed out above, much work in fact comes out directly in joules and would have to be converted from the correct into the meaningless unit.

7. It is here contended that as some reform is necessary, it had better be the full reform. Most people naturally fear a change of units, but the fear is exaggerated, as witness the speed with which we can get used to foreign currencies when we are abroad. The present conversion is one of the simplest possible, far simpler than the change from British units to metric, since it only involves one instead of a multiplicity of factors.

8. The aim of the present proposal is to get the joule into common use in numerical work with as little inconvenience as possible. It is proposed that where the numerical value of a thermodynamic quantity is given in a scientific paper it should be given in joules, kilojoules, etc., but that the author may give the value in calories in parenthesis afterwards as well. This is somewhat parallel to the method of giving metric equivalents to British mechanical units, which is used in some journals. The proposal recognizes that there are at present few who really think in terms of joules, so that it is important that the reader should be helped by also seeing quantities in familiar form. On the other hand, it must be recognized that, unless some drive is put into getting people accustomed to the joule, it will never get into use at all, and we shall be left either with the present confused system, or else with an arbitrary unnatural unit, the only merit of which is that of tradition. It is suggested that the Royal Society is the appropriate body to provide the drive in favour of the correct unit.

9. As to the field over which the proposal should apply, it is intended to be only for strictly scientific work, where there is likely to be little effect on the general public. For example, it is to be presumed that the B.Th.U. will continue to be used in the sale of gas or coal and for the more practical studies of fuels. Again the use of the calorie by dieticians has got into the public consciousness, and it would be inadvisable to change it. Other similar cases may arise.

10. The proposal was intended to apply to the publications of the Royal Society. It is to be hoped that other scientific journals will adopt some similar policy, and this one may be recommended to them, but it must obviously be for them to decide their own policy in the matter, and no exact uniformity is essential.

April 2, 1950.

OXIDATION STABILITY OF INHIBITED TRANSFORMER OILS—A CORRECTION

In the paper entitled "A Method for Evaluating the Oxidation Stability of Inhibited Transformer Oils," *J. Inst. Petrol.*, 1951, **37**, 25–39, Table II (p. 31) is incomplete. The heading over columns 8 and 9 of this table should read "B.S. 148 Oxidation Test on Oil without Inhibitor."

NOTICE TO CONTRIBUTORS

The Editor would be glad to receive short notes on technical subjects for publication in the *Journal*. Such contributions should either deal with scientific or technical subjects which, whilst of interest and permanent value, are insufficient in themselves for a full-length paper (*e.g.*, brief notes dealing with new or modified analytical procedures), or else serve as a preliminary notification of work which it is intended to report subsequently at greater length.

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Oilfield Exploration and Exploitation

Geology

532. Techniques in photogeology. L. Desjardins. *Bull. Amer. Ass. Petrol. Geol.*, **34** (12), 2284–317.—Photogeology is a youthful, but rapidly growing, specialized science. Literature on photogeology, however, has not yet fully kept pace with this growth. Published articles in undue proportion have dealt only with popular or elementary aspects of the subject, and there has been a shortage of more advanced technical articles. This has resulted in lack of appreciation, both of the potentialities and the achievements of photogeology, which are greater than is commonly supposed. Here it is attempted to present photogeology on a more advanced level.

The article deals principally with techniques and methods that are original with the writer and not previously described in the literature. It is hoped that it will be of help to those in training as photogeologists. The bibliography is selected with the principal aim of giving such students the best available foundation material.

E. N. T.

533. Trico has big gas well. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—Veon 72 in the San Joaquin Valley, California, has been completed for 1,000,000 cu. ft. gas/day from 4720 ft. Total depth was 5822 ft. C. A. F.

534. Big gasser proved in San Juan area. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-80.—1 Ute-Ignacio, La Plata County, Colorado, is reported to have flowed 40,000,000 cu. ft. from the Morrison. C. A. F.

535. Gas well completed in Morgan County, Colorado. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—Government–Smith 1, Morgan County, Colorado, on test flowed 1,000,000 cu. ft. gas/day from 5442 to 5455 ft from the Muddy sand. C. A. F.

536. Shell may have new oil, gas pool in Colorado. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—1 C. F. Green, Logan County, Colorado, topped the Muddy Sand at 4689 ft. On a 2-hr test, 4 brl of 37·9° oil were recovered from 4871 to 4897 ft. Nearest production is 2 miles away. C. A. F.

537. Revision of Pierre shale of central South Dakota. D. R. Crandell. *Bull. Amer. Ass. Petrol. Geol.*, **34** (12), 2337–46.—Recent geologic quadrangle mapping, by the U.S. Geological Survey, of parts of the Missouri River Valley in South Dakota has accentuated the need of a generally-acceptable terminology for the subdivisions of the Upper Cretaceous Pierre shale of central South Dakota. The South Dakota Geological Survey subdivided the Pierre shale in 1937, and has since made several revisions of names and of boundaries between units. This paper is a contribution to the nomenclature of several of the lower units of the Pierre shale.

In the present revision, a classification is presented that conforms to rules of the U.S. Stratigraphic Code. Three subdivisions of the Sully member, as used by the South Dakota Geological Survey, have been raised to member rank, and the term Sully has been discarded. The Agency–Oacoma zone of Gries has been redefined and renamed the DeGrey member of the Pierre shale. E. N. T.

538. Petrology of Fredonia oölite in southern Illinois. D. L. Graf and J. E. Lamar. *Bull. Amer. Ass. Petrol. Geol.*, **34** (12), 2318–36.—The Fredonia oölite member of the Ste Genevieve formation, which includes the " McClosky lime " of the oilfields, is an important source of petroleum in the Illinois basin and of stone products in extreme southern Illinois. Its petrology and geologic history therefore are significant in two commercial fields. A preliminary discussion of these matters is presented, based on a study of nineteen thin sections of specimens from quarries and drill cores. As the specimens are widely distributed geographically, conclusions drawn from data regarding them are of a general character.

Two ages of cementation and two periods of solution are described. Both primary and secondary porosity occur, although the former is more common. Twinning and undulose extinction in coarsely crystalline calcite, penetration of oölites, and disruption of oölites are evidence of pressure related to compaction, and perhaps also to diastrophism. E. N. T.

539. Louisiana's outlook bright. T. M. Winfiele. *Oil Gas J.*, 22.6.50, **49** (7), 289.—In 1949 Louisiana produced 197,877,129 brl of liquid hydrocarbons, 149,647,345 brl being from the Gulf Coast region. Gas production was 1,025,474,930 M.c.f. 1006 wells were completed, 598 giving oil and 44 gas, and 5096 wells were on production at the end of the year in South Louisiana. 2797 of the wells were flowing.

During 1949 thirty-four new fields were discovered in South Louisiana (fifteen oil, four gas, fifteen gas condensate). Thirteen of the discoveries were in the Gulf of Mexico.

The Bay Marchand discovery seems outstanding. Ten producers have been completed in Upper Miocene sands at 2800 to 5200 ft. It is on a large piercement-type salt dome discovered in 1927. De Quincy produced from Lower Miocene at 6654 to 6666 ft in the Lower Miocene on the downthrown side of a fault. Duck Lake found oil in the Miocene at 11,642 to 12,407 ft. There may be fourteen sands. East Longville is an anticline-forming closure on the downthrown side of an east–west fault. Production is from the Cockfield at about 8300 ft.

At the end of 1949 the Louisiana crude-oil reserves were placed at 1,909,769,000 brl; natural-gas liquids were 524,096,000 brl, while natural gas was 26,687,811,000 M.c.f.

Drilling offshore from Texas and Louisiana is estimated to cost $60,000,000 annually.

A table lists the 1949 discoveries with brief details. G. D. H.

540. New Mississippi discovery. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—1 Davis heirs, Jefferson County, Mississippi, on test flowed 260 brl of 44° oil in 2 hr from the Artman sand at 5535 to 5537 ft. C. A. F.

541. Two Montana wells make good showings. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-80.—1 Sawyer, Rosebud County, central Montana, on a 2-hr test recovered 3355 ft of 31·6° oil and 100 ft of oil-cut mud from 5227 to 5277 ft. Estimated production was 25 brl/hr.

State 1, 7¼ miles southeast of 1 Sawyer, on a 2-hr test recovered 90 ft of oil-cut mud, 10% oil, from 4419 to 4434 ft. C. A. F.

542. Nebraska gets two new gas discoveries. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—Macauley-Dorough Anderson 1, Cheyenne County, Nebraska, flowed 3,280,000 cu. ft. gas/day from 4662 to 4672 ft from the D sand.

Fender 1, also in Cheyenne County, produced 1,700,000 cu. ft. gas/day from 4350 to 4360 ft. C. A. F.

543. South-central Nebraska gets oil. P. C. Ingalls. *Oil Gas J.*, 29.6.50, **49** (8), 113.—1 Fischer, in Nebraska, ¼ mile north of the Kansas line, has found oil in the Lansing–Kansas City formation at 3402 to 3406 ft and 3366 to 3374 ft. After acidization 7 brl/hr was bailed. 1 Cauk, 4 miles to the north, recovered a little oil in a DST at 3428 to 3437 ft, but was later abandoned.

1 Fischer lies 6 miles north of Huffstutter in Phillips County, Kansas. The latter produces 400 b.d. from wells in the Kansas City at 3444 to 3480 ft. Both lie on the Central Kansas Uplift. This uplift is continuous with the Chadron Arch of Nebraska, where there is a thick cover of Tertiary and Cretaceous which renders surface work impossible and the results of geophysical exploration uncertain. Any oil occurring in the Palæozoic will be at 3000 to 4000 ft. G. D. H.

544. Ohio gas well completed. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-74.—A well drilled in Perry County, Ohio, had an open flow of 1,000,000 cu. ft. gas/day, from a 35-ft Clinton section, topped at 3730 ft. C. A. F.

545. Well flows 359 bbl in 15 hr. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-74.—3 Woods, Beckham County, Oklahoma, on a 15-hr test flowed 359 brl oil with 375,000 cu. ft. gas. Plugged back depth was 10,129 ft. C. A. F.

546. Northeastern Pennsylvania and central New York petroleum probabilities. B. Willard and R. E. Stevenson. *Bull. Amer. Ass. Petrol. Geol.*, **34** (12), 2269–83.—A summary of a great deal of information, previously published during the past century, on the petroleum possibilities of the plateau regions of northeastern Pennsylvania and central New York State which have, to date, been non-productive in gas or oil. It is also based on extensive field work in these areas. The area described comprises northeastern Pennsylvania, including part of the Allegheny Plateau, the Pocono Plateau, thence northward across the New York line to the Mohawk Valley and eastward to include the Catskill Mountains.

Although no gas or oil has been found in this region, nevertheless, the structure and stratigraphy offer possibilities which may warrant future exploration. At least one major unconformity and several minor disconformities are known. There are numerous facies shifts, and potential source and reservoir beds occur. Folding is recognized, but is not fully interpreted, due largely to glacial till cover and lack of geophysical exploration. E. N. T.

547. Exploration record. P. De Armond. *Oil Gas J.*, 29.6.50, **49** (8), 37.—In May the U.S.A. had 663 exploratory completions, of which 110 found oil or distillate and thirteen gas. There were relatively few rank wildcats. Most of the Illinois finds were small. Most of Oklahoma's wildcatting was in the south-central and central parts of the state, while the Forest City basin had most activity in Kansas. Wildcatting has increased in the Denver–Julesburg basin of West Nebraska and Northeast Colorado. The Glenrock oil discovery started wildcatting along the south side of the Powder River basin.

A table summarizes the results of wildcat completions in the U.S.A. in May 1950. G. D. H.

548. Gas discovery made in northwest Alberta. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—Pacific–Valleyview 1, about 50 miles south of the Normandville Devonian discovery, found gas in the Peace River (Viking). Pay was topped at 2955 ft, and on test from 2942 to 2970 ft, the well flowed a max of 3,400,000 cu. ft/day.
C. A. F.

Geophysics and Geochemical Prospecting

549. Gammatron surveys. B. Lang. *World Oil*, Nov. 1950, **131** (6), 86.—Gammatron (radioactivity) surveys can be of use in locating structures favourable for oil accumulation, and in determining the productivity of wells.

The technique was first used in 1946, and it successfully defined the Ceres shoestring pool in Noble County, Oklahoma. The highest permeability, saturation, and porosity of the field was found in the centre of a radioactivity productivity anomaly.

In the ground technique, stations are set up on a $\frac{1}{4}$-mile control. Measurements are made of the intensity of earth-radiating emanations at each point for a period of six months.
C. A. F.

Drilling

550. Engineering simplifies steam rig hook-up. E. Sterrett. *World Oil*, Oct. 1949, **129** (7), 87–90.—By careful design of inter-related units on steam-rig set-up, Housh Drilling Co. have equalled production-line assembly, *e.g.*, exhaust steam is used for furnishing boiler draft, so live steam main and the return are made up of 20-ft parallel sections which have special lugs to facilitate transportation and to carry metal walk-away. Metal pipe-rack is made up of similar and standard supports and bracing. Heavy special equipment has metal eyes near centre of gravity to facilitate lifting. Standardization in this manner simplifies assembly and reduces transportation and handling costs.
A. H.

551. Deep-water rig moves and drills in water shallower than vessel draught. G. E. McClatchey. *Oil Gas J.*, 10.8.50, **49** (14), 70.—In order to move an offshore drilling rig into locations where water depth is less than the structures draught, stabilizing pontoons have been replaced by cargo barges.
C. G. W.

552. Steel, 20,000 feet below grass roots. F. Briggs. *World Oil*, Nov. 1949, **129** (8), 94.—In the world's present deepest well a record-breaking string of 7-inch casing was set at 19,765 ft with a total weight exceeding 297 tons. To provide the necessary tensile strength an expensive alloy type (SAE 4340) was used. In deep wells it will become essential to specify steel carefully in order to avoid fatigue and other failures. There is a definite relationship between hardness and tensile strength. The " end-quench hardenability test " gives a range of hardness of a steel from surface to interior, thus allowing for areas where the surface has been cut away as in threads. Banding in steel is a structural phenomenon, the effect of which upon its strength has not yet been determined, except that, in a number of cases, failure has occurred in heavily banded stock. Photographs and photo-macrographs show typical failures and the surrounding structure. The structure and specification of various steels are discussed.
A. H.

553. American methods of drilling and investigation of the beds used in the search for oil. G. Lugol. *Rev. Inst. franç. Pétrole*, Oct. 1950, **5** (10), 318–426.—A 3200-m development well in Louisiana showed the following time breakdown : drilling 50·8%, pulling out, casing, coring, electric logging 38%, repairs, completing, etc., 11·2%. This does not include rigging-up and dismantling, which usually occupy ten days. In France and her possessions drilling may occupy about 30% of the time, but it is necessary to remember that most of the wells are wildcats. The power of the draw-works is important in the rate of running pipe. Slightly over a minute is required for addition or removal of one treble. Good organization is essential for rapid progress.

In the soft formations of Louisiana penetration rates of 7·6 m/hr are attained, while West Texas give 1·5–3·9 m/hr for wells about 3000 m deep. In terms of rock hard-

ness the rate in France should be intermediate, but is actually below 1 m/hr. Rapid mud circulation and high rotary table speeds are necessary for high-speed drilling. 20-inch or 24-inch pumps are used on the Gulf Coast, and in California table speeds exceed 250 r.p.m. In West Texas a load of 18 tons on a 6¼-inch bit has been used. Careful control of verticality is necessary in soft formations.

In Louisiana there are regulations relating to the length of surface casing, the amount of cement to be used, and the test pressure. For the production string cement must rise at least 150 m above the shoe, and in testing the pressure drop must not exceed 10% in 30 min. Squeeze cementing is used to shut off water adjacent to the oil in ordinary porous rocks, and plastics in fractured rocks.

In the U.S.A. there is a marked tendency to replace coring by electrical or radioactivity logging, mud logging, cutting analysis, drilling rate logging, etc. Both drill-stem testing and electric logging do not greatly delay drilling. Side-wall cores supplement electric log data, and if both are favourable casing may be set. Cuttings, the electric log and dip-meter provide stratigraphic data in wildcats. Log interpretation is less secure in wildcats than in exploratory wells. Quantitative interpretation is developing for exploitation wells. Mechanical coring is important in evaluating reserves. Diamond bits permit good recovery in fractured rocks.

Decentralization of authority allows decisions to be made rapidly, and enables higher executives to devote much of their time to planning the operations as a whole, but there must be centralized control. When a budget has been agreed all should be acquainted with the aims, because the obtaining of additional authorizations may be slow. Costs for a series of American wells ranged 3·5 to 100 fr/m, depending on the difficulties. Tentative figures suggest that French wells of about 3000 m cost 60 fr/m.

Most of the U/S. drilling is done by contractors. They work better than large companies, are specialists, and interested in the good progress of their operations. Generally the large companies do their own wildcat drilling. Such a system has numerous advantages. The contracts are much simpler than those in France. There are advantages in having companies which offer specialist services. G. D. H.

554. Pegasus drilling. R. F. Carlson. *Oil Gas J.*, 17.8.50, **49** (15), 80.—Major drilling problems in this area are due to extreme depths, lost circulation zones, hard-chert high-pressure gas formations, and a long salt section.

The extreme depth (12,000 ft) together with hard-chert beds make it difficult to keep straight hole. Diamond coring has been used in hard beds with some success.

Some departures are made from normal mud practice. Phosphates are used in place of caustic and quebracho below 10,000 ft. Oil emulsions have also been used below 10,000 ft.

Casing programme usually involves four strings of casing, and lost circulation raises several problems when cementing. Usual method of cementing is to pump cement as high as possible till circulation is lost. The top of the cement is located by a temp survey, the casing perforated, and cement again pumped till circulation is again lost. High proportions of lost-circulation materials have been used in many cases. C. G. W.

555. Test drilling. Anon. *Oil Gas J.*, 24.8.50, **49** (16), 170.—Recently a rig drilled 2448 ft in one-8 hr tour. 15 min of this time were occupied in running 720 ft of drill pipe and 7 hr 45 min rotating time. Average time to drill and complete a well in one area has been reduced from twenty-three to eight days. The use of jet-type drag bits is responsible for some of the success, studies of the variables in drilling being responsible for the major improvements in drilling operations. With jet bits very high drilling weights are possible, and the bits drill faster and longer, despite the high weights, deviations of wells from the vertical are no greater, and there is considerably less wear on equipment per foot drilled. Rock bits are also available incorporating the same principles, and similar improvements are anticipated in hard rock drilling. C. G. W.

556. Use of improved drilling fluids in well completion. J. E. Sherborne and P. W. Fischer. *World Oil*, Oct. 1949, **129** (7), 112–26. (*Presented before a meeting of A.I.M.E. at Los Angeles.*)—It has already been recognized that drilling fluids affect to a greater or less extent the productivity of a well. It has been found that the average pro-

ductive effectiveness ratio for wells drilled with oil-base fluids is 0·190, as compared to 0·110 with fresh-water-based mud. Three types of behaviour appear to be important: water block; interaction of mud filtrate and component minerals of the reservoir rock; plugging by suspended or colloidal matter. Assuming radial penetration, a curve is given to show the decrease in well productivity with increased water saturation. Photographs show the swelling of Montmorillonite in water and solutions of aluminium chloride. Little can be said at present about plugging. The development of improved fluids can be carried along two lines. First, fluids from which no material can penetrate the formation—oil-based and organic compounds—seem to offer the greatest success, and a material has been developed using a completely oil-soluble metal ester and other ingredients. Secondly, fluids, the filtrate from which would tend to alter the formation so that it would perhaps be more productive than in the uncontaminated state. Some success has been achieved in this direction with a polyvalent ion–starch mud. With twenty odd wells drilled with this material, there has been marked improvement over comparable water-base completions. Performance and visc curves are given.

While these special fluids are more costly to use than fresh-water muds, evidence is presented to indicate that savings in drilling and completion costs and increase in recovery make their use profitable. A. H.

557. Use of solid explosives in W. Texas. 6. R. F. Carlson. *Oil Gas J.*, 31.8.50, **49** (17), 62.—Solid explosives have been developed which are safer than, as effective as, and more economical than nitroglycerin. Two of these explosives are slower in action than nitroglycerin, whilst a third is a high-velocity explosive stable at relatively high temp. The first two of these explosives may be safely handled, as they are insensitive to impact and have successfully been drilled out with rotary and cable tool rigs. The slower development of pressure is an advantage in oil-well shooting, since the energy is used in developing and extending deep fractures rather than in pulverizing the region close to the bore hole. Since there is less pulverizing action, clean-out work is reduced. Blocks of the solid explosive are run on a wire line, the detonating bomb and tamping being similar to those used with nitroglycerin. C. G. W.

558. Radio-active and electrical logging. V. J. Mercier. *World Oil*, Oct. 1949, **129** (7), 128–32.—The basic principles, interpretation, and limitations of electrical and radioactive logs are explained in non-technical terms. A. H.

559. Completion and production techniques in unconsolidated sands. J. A. Perkins, Jr. *Oil Gas J.*, 24.8.50, **49** (16), 113.—It is believed that the majority of virgin-sand reservoirs are initially in a consolidated state. Production, with consequent loss of reservoir pressure, may create a considerable pressure differential between the producing sand and the overlying beds. If this differential is considerable, failure of the cementing material may occur, resulting in an unconsolidated sand. The formation of cavities and resulting localized faulting in overlying beds may occur by migration of unconsolidated material to the well bore. Such faulting will almost certainly result in collapsed casing and a badly damaged well. Although extreme damage is not inevitable, it is believed to result in most cases where sands become unconsolidated. The problem is investigated by a study of a representative field.

There are two methods of casing wells for producing an unconsolidated sand section. (1) Set casing above zone, complete below in open hole, using screen or consolidating material for impounding sand. (2) Set and cement casing through the producing zone, selectively perforate and impound sand within the casing. Gravel packing by pressure applications has been commonly used in such completions. The use of sand-consolidating plastics has not been justified by the proportion of successes, due mainly to difficulties in placing the plastic where required. Various types of screens are available as an alternative to gravel packing. Wire-wrapped screens are satisfactory when the openings are greater than 60 mesh. Permeable plastic screens have the advantage of being drillable, but are fragile and are plugged by small amounts of drilling mud. Two types of experimental screens are described. (1) Described as a permeable-beaded screen, uses glass beads as the screening medium. The beads are graded in size and are contained between two concentric slotted brass sleeves. (2) Uses a porous bronze sleeve as a screening medium. The sleeve is made by fusing small bronze balls together.

Procedure in a typical well completion is as follows. After the oil string is set and cemented, drilling mud is displaced by salt water containing a chemical tracer dye. The well is then perforated for production, tubing run, a packer set, and the well swabbed to establish natural flow. Wells are produced until sanding up occurs, salt water is circulated, and sand washed out. If appreciable quantities of drilling mud are found, the well is sanded up again and procedure repeated until all drilling mud is removed. An inside screen is run and sealed to the casing by a liner packer. After the screen is set the well is pumped in. During the producing life of the well the rate of withdrawal is kept as constant as possible. C. G. W.

Production

560. Trends in combating lost circulation. C. V. Sidwell. *World Oil*, Nov. 1949, **129** (8), 123.—A review of the methods and materials used in overcoming lost circulation. Compressibility curves of various materials and apparent visc curves of drilling fluids containing these materials are given. A. H.

561. Nine fully automatic leases installed in East Texas field. W. T. Nance and J. M. Payne. *Oil Gas J.*, 10.8.50, **49** (14), 58.—The manual operations involved in normal production methods are time-consuming and inefficient. In an attempt to improve efficiency, fully automatic leases have been undergoing trials.

The basic principle of control involves individual electrically-operated well valves opened and closed by means of time clocks. An automatic tank battery includes a tank switcher which allows the stock-banks to be filled in rotation automatically and equipment necessary to skip full tanks, tanks out of service, etc. Safety devices prevent overproduction or waste. All flow is stopped in case of equipment or power failure. The equipment used in the control system is described. C. G. W.

562. Application and efficiency of gas lift. C. C. Bankhead. *World Oil*, Oct. 1949, **129** (7), 160–2.—The use of high-pressure gas generally represents the most inexpensive means of artificially producing a well, especially as the depth of the well increases. Present installations range in efficiency from 30 to 90%. Efficient results cannot be obtained unless sub-surface equipment is properly installed. The operation and installation of various types of sub-surface equipment is described. A. H.

563. Gas lift evaluation and application. K. N. Mills. *World Oil*, Nov. 1949, **129** (8), 145–8.—Basically the various types of sub-surface equipment can be classified as open- or closed-type installation. In the former, the gas-lift valves are run on the tubing string without a packer or standing valve and without restrictions between tubing and casing. It is limited to wells with a relatively high bottom-hole pressure. In the closed-type the lower end of the tubing is fitted with a standing valve and the space between the tubing and casing is closed off with a packer above the production formation. As a practical rule, the min gas pressure should be at least 100 p.s.i. per 1000 ft of lift.

Setting distance (S) of top valve below the static fluid level can be calculated by

$$S = \frac{P_1 + P_2 - 100}{W\left(1 + \frac{A_1}{A_2}\right)}$$

or with wire-line-controlled valves.

$$S = \frac{P - 100}{W\left(1 + \frac{A_1}{A_2}\right)}$$

spacing of valves (D) is given by

$$D = \frac{P_1 + P_2 - 100}{W}.$$

The efficiency of a gas-lift system (E), assuming isothermal expansion can be evaluated, is given by

$$E = \frac{350\ BGL}{4860Q \log P_2/P_1}.$$

An alignment chart, for determining efficiencies, is given.

P = casing pressure (p.s.i.).
P_1 = initial pressure in casing (p.s.i.).
P_2 = increase in pressure used to operate valve (p.s.i.).
W = static fluid gradient (p.s.i/ft depth).
L = depth to point of input of gas (ft).
Q = Quantity of gas reqd. to lift B.
A_1 = area of annulus (sq. in.).
A_2 = area of tubing (sq. in.).
B = barrels of oil produced.
G = sp. gr. of oil produced.

A. H.

564. Reservoir reconditioning conserves water-drive energy. F. R. Cozzens. *World Oil*, Oct. 1949, **129** (7), 183–4.—Field practice shows that under average conditions only a small percentage of the driving energy pressured to an input is actually expended against the oil bank. A significant part escapes through abandoned shot-holes, leaks in packers, and through beds of shale. In these places contaminated water is often contacted, which then has corrosive and plugging effects. Packers, particularly the shoulder, must be carefully placed, otherwise productive zones may be sealed off or the flood water may contact shales providing chemical reactions. A method of setting packers and sealing off abandoned producers is described. During the repair of producing wells the operator can, by analysis and observation, learn much about the origin of encroaching water. A. H.

565. Conditioning water for secondary oil recovery in Appalachian fields. J. N. Breston. *Oil Gas J.*, 24.8.50, **49** (16), 159.—The objectives in water treating are: (1) highest rate of water injection with minimum effort, (2) prevention of corrosion of water-handling equipment, (3) improving the effectiveness of water in displacing oil from the formation. Little is known of factors affecting the third objective, and primary requisites of an injection water are freedom from suspended matter and chemical stability. Many raw waters are suitable if oxygen is excluded and microbiological growths are controlled. Generally, however, all waters are treated in case chemical stability has been upset during handling of the water. Such treatment may involve: (1) lime or caustic to eliminate manganese, iron, and hydrogen sulphide (pH control is effected by subsequent addition of HCl); (2) settling in tanks. Flocculating agents may be added to assist settling; (3) filtration by gravity or pressure through filter-beds; (4) addition of complex phosphates to prevent precipitation of iron or calcium; (5) chlorine, copper sulphate, etc., for control of algæ, fungi, and bacterial growths.

Such a treatment results in a reasonably stable water having slight scale-forming tendency. Typical practices in effecting such a treatment are described.

Some operators are in favour of maintaining a slightly corrosive water, with oxygen strictly excluded, rather than risk the precipitation of material from water with a scale-forming tendency. This is usually effected by an amine-type treatment.

Alkyl and aryl high-mol.-wt. amines and amine salts and some ethylene oxide–amine condensation products have been used to control excessive acid corrosion and the growth of microbiological organisms. These are effective in concentrations of a few p.p.m., even in the presence of 1 to 2 p.p.m. of dissolved oxygen. Filtration is the only additional treatment given to amine-treated waters.

Better and faster results are obtained if the water is cleaned up by slug treatments of hypochlorite solution prior to amine treating. Initial amine treating is done with concentrations of 25 to 40 p.p.m., and this is cut down when a residual of amine is maintained at the farthest ends of the water-input system. Results obtained with the costs of amine treating are discussed.

References are appended. C. G. W.

566. Chemical treatment of flood waters used in secondary oil recovery. V. P. Gregory, C. R. Groninger, and J. H. Prosick. *Oil Gas J.*, 31.8.50, **49** (17), 74.—In addition to inhibiting corrosion and decreasing plugging of sands, secondary recovery waters should preferentially wet sand surfaces. If the surface tension of the aqueous phase is reduced, more oil and less water will flow into the producing well.

Amines and amine salts are now being used for corrosion inhibition, and bactericidal chemicals are well established. In addition, tests have been made on the interfacial tensions of materials, and an attempt has been made to find an inorganic chemical to combat corrosion by dissolved oxygen. The tests were all laboratory tests, and have not yet been confirmed by field experience.

To stimulate flood waters, acid solutions of hydrogen chloride, sulphuric acid and hydrogen sulphide and also alkaline solutions were prepared. Results of the tests are described and tabulated.

It is concluded that a combination of three chemicals is necessary for complete chemical treatment. These chemicals are an economical, inorganic antioxidant; a quaternary ammonium compound, and a wetting agent. The most effective combination was found to be Arquad 2C 5 p.p.m., sodium nitrite 50 p.p.m., Ethofat 142/15 or Ethomeen S/20 5 p.p.m. The proprietary chemicals are produced by the Armsur Chemical Division. C. G. W.

567. Requirements of subsurface injection water in oil production. K. H. Andresen and F. T. Gardner. *Oil Gas J.*, 7.9.50, **49** (18), 72.—Effects caused by poorly-conditioned injection water are: (1) plugging by suspended matter; (2) mechanical failure of equipment due to corrosion; (3) plugging by salts precipitated by chemical action; (4) plugging by growths of bacteria and algæ; (5) swelling of clay minerals in contact with injection water. Each of these factors is dealt with, and the methods by which they can be combated are described. Operating problems involved in a water-treating project are outlined, and it is pointed out that practical solutions are obtained by effecting a suitable compromise between conflicting factors. To illustrate that such compromises are necessary, the advantages of maintaining a high pH, and of aeration as part of the treating system are outlined.

References are appended. C. G. W.

568. Laboratory water drives in oil sands. H. M. Ryder. *World Oil*, Nov. 1949, **129** (8), 172–6.—Very great care must be taken in carrying out laboratory tests to determine the most effective water-flooding procedure. The importance of various factors in simulating field conditions is discussed. A. H.

569. Methods of treating water for flooding purposes. A. R. Ellenberger. *Petrol. Tech.*, Aug. 1950, **2** (8), 6–8.—Carbon dioxide and hydrogen sulphide may be dissolved in ground waters, and their equilibrium with other compounds is a function of the temp and pressure, and this equilibrium is disturbed when the waters are brought to the surface. However, there are some waters in which there is no appreciable disturbance of equilibrium on bringing to the surface, and no iron needs to be removed. However, the growth of bacteria, algæ, and fungi must be prevented. Chlorination, coagulation, sedimentation, filtration, and stabilization are necessary in this case.

In carbonate waters there is often more carbon dioxide than can be held in equilibrium by the calcium carbonate. This " aggressive " carbon dioxide acts as an acid which will attack iron or calcium carbonate. The treatment needed is dependent on the compounds present and the temperature. Sometimes hydrated lime is used to adjust the alkalinity; sometimes caustic soda. Calcium carbonate may or may not be precipitated by the treatment. Complex phosphates are used to control stability.

When iron and manganese bicarbonate are present, loss of carbon dioxide leads to the formation of hydroxides by hydrolysis, with subsequent oxidation to hydrated oxides, which yield gelatinous precipitates. Soluble iron and manganese compounds support the growth of certain bacteria. Lime or soda treatment is needed, while oxygen is excluded, and chlorine is added as an oxidizing agent which also prevents organic growth.

Aeration will remove hydrogen sulphide but creates other problems, but chlorine will convert hydrogen sulphide to sulphates. After-treatment by complex phosphates is essential.

The use of produced waters as flooding water removes disposal problems. Cascading or other movements which facilitate the solution of oxygen should be avoided. A small amount of oxygen is preferably de-activated by use of sodium sulphite. G. D. H.

570. Vapour–liquid equilibrium data on the system natural gas–water–triethylene glycol at various temperatures and pressures. J. A. Porter and L. S. Reid. *Petrol. Tech.*, Aug. 1950, **2** (8), *A.I.M.M.E. Tech. Paper No.* 2848, 235–40.—Most gas companies require the water-vapour content not to exceed 7 lb/10^6 cu. ft., hence most gas must be dehydrated. Nowadays dehydration may be necessary at pressures up to 2000 p.s.i., and small inexpensive units are now required. Diethylene glycol–water solutions have been used for dehydration at pressures up to 1200 p.s.i. At pressures of 300 to 500 p.s.i. triethylene glycol has been found to give a substantially greater dew-point depression, and experimental work has been carried out with 95% triethylene glycol and 5% water solution in relatively nitrogen-free natural gas at pressures of 500 to 2000 p.s.i. and temp of 60° to 100° F. Details of the laboratory technique and materials are given.

It was found that the equilibrium dew-point depression in a triethylene glycol dehydration system operating at a specific pressure was a function of contact temp only over the range of temp used. The solubility of natural gas in 95% triethylene glycol–water solution varied with pressure, but not linearly, while temp had a negligible effect on gas solubility. The practical pressure limit for natural-gas dehydration using 95% triethylene glycol–water solutions is about 1500 p.s.i. Dew-point depression diminishes rapidly above 1000 p.s.i., but as high as 1100 p.s.i. the depression with 95% triethylene glycol–water is greater than for diethylene glycol–water solution of the same strength.

Diethylene glycol decomposes at 328° F, and therefore the max concentration attainable without decomposition is under 97%; triethylene glycol decomposes at 404° F, and the concentration can be raised to 99% without decomposition.

G. D. H.

571. Analysis of fractured limestone cores. F. C. Kelton. *Petrol. Tech.*, Aug. 1950, **2** (8), *A.I.M.M.E. Tech. Paper No.* 2913, 225–34.—The porosity and fluid saturations of sections of limestone cores were determined by a modified Dean–Stark method after initially bringing the samples to 100% liquid saturation by a vacuum technique in which the gas in the core was replaced by water. Subsequent extraction using toluene took three days to three weeks, the average time being a week. These operations, together with a subsequent water saturation, afforded porosity and oil-saturation data. The permeability was then measured by clamping on the cylindrical surface rubber gaskets with rectangular openings so that air could be caused to flow mainly across the core. When an experimental determined correction for flow out through the ends had been applied, the permeability was calculated for the direction which had been arranged to be that of the principal fracturing. Next a measurement at right angles to the direction of fracturing was made by moving the gaskets round through 90°.

For dolomites the logarithm of the permeability was roughly proportional to the porosity; for fractured limestones the highest max permeabilities were in the porosity range 4 to 10%.

Comparisons are made with the results obtained by conventional analysis of the same specimens. Further comparisons show that the matrix porosity ranged 60 to 94% of the total pore space for a series of Ellenburger cores, while the matrix permeability might be as low as 0·05% of the max permeability or 3% of the min permeability, while the ratio of the max and min permeabilities could be as high as 340.

A modified method of analysis is proposed because the special technique is slow.

G. D. H.

572. Liquid–liquid displacement in porous media as affected by the liquid–liquid viscosity ratio and liquid–liquid miscibility. J. P. Everett, F. W. Gooch, and J. C. Calhoun. *Petrol. Tech.*, Aug. 1950, **2** (8), *A.I.M.M.E. Tech. Paper* No. 2787, 215–24.—Two sets of experiments have been made on liquid displacement from slightly cemented sand. In one sugar solutions were displaced by other sugar solutions or water; in the other oils were displaced by water. In both cases the issuing liquid was wholly the original

liquid until 0·4 to 1·0 pore volumes of liquid had been expelled, and thereafter it was a mixture or solution in which the content of the original liquid rapidly declined. For the sugar solutions and water the higher the ratio of the visc of the displaced to the displacing liquid the lower the displacement before break-through. The same was true for oil and water. The greater the pressure differential causing flow, the lower the displacement at break-through for the solutions. 100% displacement with solutions required one pore volume of flow for zero visc ratio and 4 pore volumes for a visc ratio of 9, and the relationship was linear. Up to 91% recovery was obtained with water displacing oil.

It is considered that viscous rather than interfacial forces dominate the displacement mechanisms. G. D. H.

573. Interpretation of capillary pressure data. W. R. Purcell. *Petrol. Tech.*, Aug. 1950, **2** (8), 11–12.—If displacing fluid advances through a pore opening of the form of an anchor ring, then for values of the contact angle other than zero it is shown that the pressure within the displacing fluid can be greater, equal to, or less than the pressure in the fluid being displaced for suitable stages of advance. Curves have been derived to show the pressure relations for various contact angles at different points within the anchor-ring pore. The hypothetical capillary pressure curve for a three-dimensional array of anchor-ring pores has been derived from the foregoing data. The presence of an irreducible water saturation is indicated on general grounds when oil displaces water, while an irreducible oil saturation will arise if pressure conditions are reversed so that after reaching the irreducible water saturation oil is displaced by water. These irreducible oil or water contents are attributed to bridging.

G. D. H.

574. Secondary recovery in Louisiana. J. H. Tillery. *World Oil*, Nov. 1950, **131** (6), 155.—Problems of secondary recovery in Louisiana differ from those in Oklahoma and Kansas, where reservoirs are older, shallower, and more consolidated than in the Gulf Coast area. Successful recovery demands that the entire reservoir be included in the secondary recovery project.

Gas injection was first used in Louisiana in the Homer Pool, Claiborne parish, which was discovered in 1919. As a result of field-wide repressuring, from 1938 to 1943 there was a constant increase in daily average production. Prior to repressuring, average daily production of the field was 2024 b.d., compared with 2678 b.d. in Aug. 1943.

There are now pressure maintenance projects in about eighteen oil and/or gas pools in the state. These include ten gas-injection, eight water-injection, and two combination water- and gas-injection programmes. It is estimated that secondary recovery will increase ultimate recovery by 46·4%.

A pressure-maintenance programme is now operating in the Longville field, Beauregard Parish. Production was found in the Long Bell No. 3 sand (Cockfield) at about 820 ft subsea in 1947. Development was on 40-acre spacing. Of eighteen wells drilled, five were non-productive. Productive area is approx 880 acres, carrying thirteen producers averaging 1200 : 1 solution G.O.R. Production rate in Nov. 1948 was 1500 b.d., 40% less than the field's initial production of 2500 b.d. It was estimated that a pressure-maintenance programme would increase the ultimate yield by 2–4 million brl, and in Nov. 1948 a water-drive programme was initiated under unit agreement. Studies in 1949 showed that the reservoir pressure decline had been stopped, and that the producing G.O.R. had been reduced by over 15%.

A structure map of the Long Bell 3 sand and diagrams showing the production performance of the field are included. C. A. F.

575. Larimore gas injection project. M. A. Remke. *World Oil*, May 1950, **130** (6), 164.—The Larimore field, Young County, Texas, was discovered by E. I. Remington 1 in 1930. Initially wells were flowing, but after rapid development of the shallow Larimore sand, the pressure declined, and most wells were on pump in 1932.

There are two Pennsylvanian Cisco pay sands—the Taach at about 650 ft and the Larimore at approx 700 ft. The Larimore is the more important reservoir, and has been repressurized.

Pressure maintenance commenced in 1931 before the field was fully developed.

Two small compressors were used, averaging 50 M.c.f/day each. These operations were expanded in 1933, and in 1934 and 1935 production remained relatively constant at approx 190,000 brl/yr. Operating practice was revised in 1942, when the injection vol averaged 320 M.c.f/day. G.O.R. was 1900 : 1, and this has now increased by 50% over the 1942 figure. A new compressor of 800 M.c.f/day capacity has been installed.

Cumulative production of the field to the end of 1948 was 2¾ million brl or 56·5% of the calc stock tank oil in place. The net oil recovered by gas injection is estimated at 21% of the stock tank oil in place.

Reservoir characteristics of the pool are described.

Structure and isopach maps of the Larimore sand, and a chart showing reservoir performance and production history, are included. C. A. F.

576. Stage separation of natural gas from crude oil. C. M. Edghill. *Birm. Univ. Chem. Engr*, 1950, **2**, 30–4.—A review of the theory and practice of stage separation of gas from crude oil. It is stated that the final degree of the vaporization of crude oil as it is produced from the well is controlled by the conditions to which it is subjected as well as its composition. The extreme limits are represented by flash and differential vaporization. The latter provides max volume recovery of usable hydrocarbons in the liq phase, and is brought about by a gradual decrease of pressure at const temp as gas is removed from the system. In order to approach differential vaporization with continuous operation but without excessive cost, a differential flash-vaporization method has been developed, the degree of approach to differential vapour being controlled by the number of stages and the selection of optimum pressure for each stage. Two-, three-, and seven-stage systems are briefly considered. Thirteen references. D. F. J.

577. The water vapour content of essentially nitrogen-free natural gas saturated at various conditions of temperature and pressure. E. L. McCarthy, W. L. Boyd, and L. S. Reid. *Petrol. Tech.*, Aug. 1950, **2** (8), *A.I.M.M.E. Tech. Paper No.* 2914, 241–2. —A series of graphs present experimental data on the max water content of essentially nitrogen-free natural gases for temp of −60° to 280° F and pressures from atmospheric up to 6000 p.s.i.a. The range of water contents is 1 lb to 60,000 lb per million cu. ft. at 14·7 p.s.i.a. and 60° F.

The data are of value in connexion with high-pressure gas wells, the operation o high-pressure pipelines, and the design of dehydration facilities. G. D. H.

578. Well remedial work. W. B. Hopkins. *Oil Gas J.*, 31.8.50, **49** (17), 69.—The factors to be considered before instituting remedial work are discussed.

(1) The production performance of the well and the reservoir in which it is completed must be studied. Oil-, gas-, and water-production data with reservoir-pressure measurements may indicate suitable remedial operations. Geological records are of value in supplementing production records.

(2) The work necessary to restore the well to production. Such work may be classified as : (i) recompletion in the same reservoir from which it is now producing, (ii) recompletion in a reservoir penetrated by the well and cased off, (iii) recompletion in a deeper reservoir by deepening operations.

Recompletion in the same reservoir often involves only mechanical repairs. The equipping of wells for artificial lift should be considered after completing such mechanical repairs. The factors involved in recompleting in different zones are discussed and the importance of accurate depth measurements emphasized. Other factors involved are obligations under lease agreements and drainage of wells, since it may be possible to produce the oil from another well on the lease and recomplete the well in another zone.

Calculations of costs on a workover job are analysed and a sample table shown. C. G. W.

579. Equipment installation in Surack Over field, Arkansas. W. C. Best. *Oil Gas J.*, 7.9.50, **49** (18), 64.—In a field where production operations were inefficient, it was demonstrated that from seventy-two to seventy-nine wells with modern electric pumping units recover the cost in just over three years.

Dynamometer surveys were carried out on fifty-seven of the wells. The factors involved in the selection of equipment are reviewed. Advantages claimed for electrical installations are: (1) lower initial investment; (2) lower maintenance costs; (3) pumping loads easily measured; (4) proper counterbalancing simplified; (5) less down-time due to prime-mover trouble. Disadvantages are: (1) inflexibility of electric pumping equipment; (2) motor size must be closely related to pumping load; (3) cost of electrical energy cannot compete with reasonably-priced fuel on fuel costs alone.

C. G. W.

580. Field men devise stuffing-box. W. H. Fowler. *World Oil*, Nov. 1949, **129** (8), 150.—Shell Oil Co.'s field men have developed a satisfactory sucker-rod pump stuffing-box, the total cost of which is less than $8. Photographs show the complete assembly and the component parts. A. H.

Oilfield Development

581. Exploration up 13·3 percent for year. Anon. *World Oil*, Nov. 1950, **131** (6), 94.—767 exploratory wells, of which 147 found pay, were drilled in the U.S.A. in Sept. 1950, bringing the total for the year to 6295, or 13·3% more than in 1949. Seventy new oil fields and twenty-one new pays were found during the month.

Tables show the results of exploratory drilling in the U.S.A. in Sept. 1950 and the first nine months, 1950–1949, by districts, and production data on the new oil, distillate and gas fields and new pays discovered in Sept. 1950. C. A. F.

582. Treasure in the depths. E. Adams. *Petrol. Engr*, Dec. 1950, **22** (13), A-33.—The first well below 12,000 ft in the U.S.A. was drilled in 1935. Six wells were drilled below 12,000 ft in 1937, and two fields were found below 13,000 ft in 1938—the Wasco field, California, and the Large field, Louisiana. Subsequent deep drilling was unsuccessful: in 1944, thirty-eight deep wells were dry. Since then, deep drilling has been more successful. In 1949, of 226 deep wells drilled, nineteen found production.

832 deep wells have been drilled in fifteen years, costing approx $300 million, varying from $87,00 to $1,600,000/well. Use of giant rigs has reduced drilling times. The Pacific Creek well had a 192-ft derrick with a capacity of 1,100,000 lb.

Outside the U.S.A. only twenty deep tests have been made. The Canadian 1 Walter Marr found production at 12,768 ft, and the German Holstein 4 was drilled to 12,726 ft in 1938. There are two French wells below 13,000 ft. Two wells in Baku are reported to be below 12,000 ft, and there are deep wells in Papua, the West Indies, and Venezuela.

Cumulative production from these deep wells has more than paid for the cost of drilling.

Tables show the deep wells drilled in the U.S.A., and production data on fields below 12,000 ft. C. A. F.

583. California water-flooding practice and research. W. H. Somerton. *World Oil*, Oct. 1949, **129** (7), 164–72.—With the rapidly depleting oil reserves of California, it will become necessary to resort to secondary recovery. There are many problems to be investigated; the irregular and often steeply dipping structures intersected by numerous faults; the thick, lenticular, interbedded shales and argillaceous sands and sandstones; lack of water in some areas, etc. There are also legal difficulties to be overcome. These problems and the type of research programme needed are discussed.

A. H.

584. Oil exploration in Florida during 1949. H. Gunter. *Oil Gas J.*, 22.6.50, **49** (7), 310.—Twenty-four wells were completed in Florida in 1949, three being producers at Sunniland, where there are now thirteen oil wells. Sunniland's cumulative production at the end of 1949 was 441,720 brl.

Florida's first test was drilled in 1900, and seventy-nine were drilled to 1939; 154 tests were drilled between 1940 and 1949. Sunniland was opened in 1943 with production at 11,535 to 11,597 ft. In 1949 no successful wells were drilled outside Sunniland, and there were no outstanding additions to geological knowledge.

G. D. H.

585. Oil and gas developments in Kansas during 1949. J. B. Steele and J. H. Page. *Petrol. Tech.*, Aug. 1950, **2** (8), 95–117.—In 1949 Kansas' oil production averaged 274,422 b.d.; 1687 oil wells were completed, 424 gas wells, and 1294 dry holes. The gas production in 1949 was 264,225,963 M.c.f. 60% of all the completions were in seven counties, six of which were on the Central Kansas Uplift. The overall average depth of the completions was 3300 ft. 540 exploratory tests were completed, 16·5% being successful. Eighty-two new oil pools and seven new gas pools were opened.

Tables list the fields with data on oil and gas production, wells, type of oil, producing formation, etc., and provide salient data on important wildcats completed in 1949.

Geophysical activity was a third below the 1948 level. At the end of 1949 there was one gravity meter crew working in Ness County, seven seismic crews scattered from Sumner County to Sheridan County, seven core-drill crews at work from Hamilton County to Wabaunsee County, and seventeen crews doing surface work in Wabaunsee County. G. D. H.

586. Oil and gas developments in east and east central Texas during 1949. J. S. Bell and B. W. Evans. *Petrol. Tech.*, Aug. 1950, **2** (8), 118–30.—In 1949 east and east central Texas produced 139,700,000 brl of oil, forming 18·7% of the total Texas output in 1949. 186 wildcats were completed, opening seventeen zones in fifteen new fields, and a new zone in each of eight existing fields. 1000 crew-weeks of geophysical work were spent, and about 500,000 acres of new leases were acquired.

Woodbine reservoirs gave 84·4% of the 1949 production, while the Paluxy gave 7·7%.

6,800,000 brl of condensate was produced, nearly half being from Carthage. 928 wells were drilled in proven fields, 775 giving oil, and forty-six gas. 469 oil wells and twenty-one dry holes were drilled in the East Texas field.

Tables give the monthly production and average reservoir pressure for the East Texas field; production, well, and reservoir data by fields; data on the important 1949 wildcats, and 1949 and cumulative production for the Woodbine and Paluxy by fields. G. D. H.

587. Mexico heads for drilling record. J. J. Slattery. *World Oil*, Nov. 1950, **131** (6), 304.—1950 was Mexico's most active drilling year. About 180 wells were drilled, compared with 158 and eighty in the previous two years. In the first eight months of 1950, of the 114 wells drilled, 61% were producers. Most wells drilled were adjacent to old fields in the southern district, such as the Alazan field.

A new deep limestone zone has been found on the southeastern edge of the Poza Rica structure (the Escolin field).

A wildcat which discovered the President Aleman field near Poza Rica initially produced 230 b.d. C. A. F.

588. Completions record virtually certain. Anon. *World Oil*, Nov. 1950, **131** (6), 68.—32,384 wells were drilled in the U.S.A. in the first nine months of 1950, 12·3% more than in the same period of 1949. 3945 wells were completed in Sept. 1950, slightly more than in the previous month.

Tables show well completions in the U.S.A. in Sept. 1950, and cumulative for the year, by states or districts. C. A. F.

589. Alberta gas. D. M. Duff. *Oil Gas J.*, 29.6.50, **49** (8), 47.—Three companies are seeking permission to build a gas pipe-line westwards from Alberta. All have now obtained charters from the Canadian Parliament. Permits to export gas from Alberta are now being sought. A decision may be made early in 1951. Two companies have made detailed proposals. Westcoast's route is all-Canadian. The more southerly route of Northwest Natural would be expected to open larger markets. The former is planned to transmit 155,000,000 cu. ft/day by 1955; the latter would average 205,000,000 cu. ft/day. It is claimed that the southern route would provide cheaper gas for the customers and a better price for the producers.

Alberta's proved and probable reserves are estimated at 5,042,000,000 M.c.f. and potential reserves 7,138,000,000 M.c.f.

A map shows the existing and proposed gas pipelines. G. D. H.

590. International. Anon. *Oil Gas J.*, 29.6.50, **49** (8), 53.—A third producer has been completed in the Lacq area of the Lower Pyrenees in France.

A 7750-sq mile airborne magnetometer survey has been completed in north central Tunisia. The survey lasted thirty days.

Venezuelan oil production attained a peak of 1,565,114 b.d. on June 12, 1950. G. D. H.

591. Po Valley production up over 1949 period. Anon. *World Oil*, Nov. 1950, **131** (6), 304.—8000 tons (7⅞ brl/ton) were produced from the Po Valley, Italy, in the first eight months of 1950. 1949 production averaged 8000 tons/month.

Production has been found in the Ponte Garbese zone at about 8500 ft in the Nori area. C. A. F.

592. Netherlands survey made. Anon. *Petrol. Engr*, Dec. 1950, **22** (13), B-78.—Six exploratory rigs are now operating in the Netherlands, where a survey of the entire country is nearing completion.

Estimated production from the Schoonebeck field for 1950 is 700,000 metric tons, or 30% of domestic requirements. C. A. F.

593. Japan looks up. D. M. Duff. *Oil Gas J.*, 29.6.50, **49** (8), 50.—Daily output has risen to about 5700 b.d., largely due to the Yabase developments. Seven Pacific coast refineries have been rehabilitated, and about 25,000 b.d. is expected to be processed in 1950–51. Thirty-four producers were completed out of sixty-three wells drilled in 1949. 6,540,000 brl were added to reserves, making the total 21,067,000 brl. Zone VIII at Yabase provided the greatest addition to reserves.

There have been improvements in drilling and cementing techniques.

Dry gas production averaged 4,417,000 cu. ft/day in 1949, while gas produced with oil averaged 2,220,000 cu. ft/day. G. D. H.

Transport and Storage

594. Closed system layout for intermediate station. H. L. Drake. *World Oil*, Nov. 1949, **129** (8), 212–14.—On pipelines it is desirable to have as few storage tanks as possible. This is not always possible, due to different rates of flow coming in and going out of a station. A diagram is shown of Stanolind Pipe Line Co's Cozard Station, which, using automatic controls and one 5000 brl spill tank, offers possibilities for closed-system operation. A. H.

594a. The transcontinental gas pipe line. J. E. Kastrop. *World Oil*, Nov. 1949, **129** (8), 187–91.—A discussion of the financing and present state of the 1876-mile 30-inch gas line being laid from the lower Rio Grande Valley to Greenwich, Conn., at an estimated cost $242 million. A. H.

595. The Great Lakes Pipe Line Company's dispatching table. E. Sterrett. *World Oil*, Nov. 1949, **129** (8), 194–6.—A description is given of the circular dispatching tables and charts used by the Great Lakes Pipe Line Co. for recording and controlling the flow of material through their pipelines. A. H.

596. New controls improve operations in densely populated areas. G. M. Wilson. *World Oil*, Nov. 1949, **129** (8), 199–202.—Automatic controls were recently installed in Richfield Oil Corps' 10-inch crude line to protect built-up areas from damage due to breaks, leaks, etc. Where it passes through heavily built-up areas, a cathodic protection system has been installed on the line to guard against possible failure due to galvanic action of the soil. A. H.

597. Forces in pipe bends from expansions. F. E. Wolosewick. *Refiner*, 1950, **29** (10), 103–8.—A method of calculating stresses set up in pipes due to expansion, which may cause distortion of flanges, etc., and lead to unsatisfactory and unsafe working. A mathematical analysis of the problem is made using Castigliano's

" Theorem of least Work " and further working equations obtained by analogy with bent columns. (Method of Professor Cross, " Column Analogy," Bulletin No. 215, University of Illinois.) An illustrative example is given, showing that the computation is not very tedious. Values of moments of inertia of various pipe bends about axes through their centroids are given to help with solutions. R. W. G.

598. Pressure drop for oil–gas mixtures in horizontal flow lines. N. Van Wingen. *World Oil*, Oct. 1949, **129** (7), 156–8.—Martinelli and co-workers suggested a simple and direct method of calculating pressure drop for two-phase two-component flows. The author had collected empirical pressure-drop data for 3-inch flow lines from actual oilfield operations. Flow-line lengths ranged from 425 to 3000 ft and flows from 59 to 1200 b.d. Actual pressure drop was plotted with that calculated by the Martinelli equations and quite good agreement was obtained. At low rates of flow the difference is less than 1 p.s.i/1000 ft. At higher rates the divergence is greater, but computed pressure drops are higher than observed, and therefore the former are safe to use in design work. A. H.

599. Submerged—arc welding speeds double jointing 30-inch pipe in the field. J. E. Kastrop. *World Oil*, Nov. 1949, **129** (8), 226–32.—Contracts to double-joint a total of 291 miles of the Transcontinental Gas Line by this process have been let. The equipment, which is transported easily from yard to yard, was set up in leased land near railroad sidings and as near as possible to main pipeline. Average number of welds made during a day ranged from eighty-five to ninety, as compared with the sixty usually made by a larger crew of hand welders. With such machine welding the human element is excluded, thus insuring the same quality weld throughout and so less inspection is required. The process and equipment are described with the aid of photographs. A. H.

600. Welding the Finnart pipeline. Anon. *Mech. World*, 29.12.50, **128** (3337), 605.—Details are given of the 54-mile arc-welded pipeline extending between Grangemouth on the east coast of Scotland and Loch Long on the west coast, which is now under construction for the Anglo-Iranian Oil Company. The line is for conveying crude oil from Loch Long to the refinery at Grangemouth. The pipe used is of 12-inches diameter, $\frac{3}{8}$-inch wall thickness, and is supplied in 35-ft lengths. It is delivered with the ends ready prepared to an included angle of 60° and $\frac{1}{8}$-inch root face and ready coated with bitumen to within 6 inches of the end of each pipe. The welding procedure is given and illustrations reveal how this is carried out. When approximately 1 mile of pipe has been welded, the ends are blocked off and the pipe is put under 100 p.s.i. test pressure. One in every twenty joints is inspected by trepanning a sample from the joint and the entire weld viewed inside the pipe using an Introscope. By this means the trepanned sample is checked and examined for faults such as piping, lack of penetration, and slack inclusion, etc. The pipe is then painted with bitumen and a bitumen mould formed round the pipe, after which it is lowered into the trench. Before filling the trench, cathodic protection wires are placed at about 300-yd intervals, thermit welding being used to fuse wires to the pipe. A. S.

601. Tapline's pump station. P. Reed. *Oil Gas J.*, 28.12.50, **49** (34), 71.—The fourth and final article of the series concerns the six pump stations for the initial programme of the Trans-Arabian pipeline system. Turbines, engines, controls, instrumentation, and dust protection for transporting a full load of 315,000 b.d. through the 1068-mile 30- and 31-inch crude oil line from Abaiq field in Saudi Arabia to Sidon, Lebanon, are dealt with. G. A. C.

602. Portable pipe line boosters. F. B. Crandall. *World Oil*, Oct. 1949, **129** (7), 195–6.—A portable skid-mounted booster pump has been used by Phillips Petroleum Company to increase production in their 8-inch products pipeline. There are four such units installed each driven by a 260-h.p. (continuous) diesel engine and max daily rate has been increased from 25,600 to 30,000 b.d. A. H.

603. Electric and gas-turbine drives for oil and gas pipe lines. F. L. Kaestle. *World Oil*, Nov. 1949, **129** (8), 204–11.—The gas-turbine engine has promise of the widest

application on large gas trunk lines. Studies now indicate that the lower economic limit of gas-turbine ratings is 2000 h.p. For reasons of flexibility 5000–7000 h.p. is probably the largest practical drive required even on the largest gas lines. Three types of gas turbine are described, viz.: simple, intermediate, and complex cycle. The efficiencies and cost of these are approx: 17%, 25%, 30%, and $75, $85, $100/h.p. respectively. The first two types do not require water. Where waste heat is required, use of the exhaust gas improves the overall efficiency. Apart from comparative costs of fuel and power, electric-motor drives have the following advantages: installed electric-station costs are the lowest for any type of available drive, maintenance and operating costs are low, and it should be possible to have remote supervised, unattended pump-stations. Local conditions, however, often govern the type of drive to be installed, and on a long span this will vary from station to station. A. H.

604. Mechanical seals effective on main-line pumps. M. J. Darney and W. W. Holt. *Oil Gas J.*, 4.1.51, **49** (35), 57.—The Plantation Pipe Line Co. has developed and service-tested at Doraville, Ga., a seal for centrifugal pipeline pumps with shaft dia of 2½-inch rotating at 3600 r.p.m. on pressures up to 850 p.s.i. The seal replaces the soft metallic packing conventionally used between the pump case and rotating shaft, and operates satisfactorily on all refined petroleum products from fuels to liquefied petroleum gases. Double oil, lubricated single, and single unlubricated partially balanced seals were investigated. Several exceeded 10,000 hr of trouble-free operation, and any failures were amply preceded by a warning leakage. G. A. C.

605. Transport in Venezuelan operations. G. F. Kendall. *Oil Gas J.*, 14.12.50, **49** (32), 76.—Organization of transport by Socony Vacuum Oil Co. in Venezuela over roads ranging from fair hard surfaced to jungle tracks is described. A chart shows the layout of the transportation division.

A driver-training programme inaugurated in 1949 includes conventional motor-care and driving tests, and use of traffic safety films. Promising young Venezuelan personnel receive special training.

Expenditure is controlled by adequate experienced field supervision, control of productive time and output, and recording of equipment utilization.

Where economic, hired transport is also used. G. A. C.

606. Portable automatic sampler. W. E. Roads. *Oil Gas J.*, 7.12.50, **49** (31), 89.—A special-purpose device which has been designed to take a series of samples throughout a large pipeline system is described.

It is portable, easily made and installed, completely self-contained, and continuously bleeds crude oil from the pipeline, allowing sampling at any location where oil is flowing under pressure. Limitations include loss of portion of light ends to atmosphere, variations in sample rate due to marked variations in visc of crude oil; and difficulty in making adjustments for large variations in sample rate; nor can B.S. & W. determinations be made.

A schematic arrangement shows the equipment, which includes strainer, pressure-reducing valve filter, diaphragm-control valve, containers, and 6-volt battery.

G. A. C.

Refinery Operations

Refineries and Auxiliary Refinery Plant

607. First liquid feed T.C.C. unit completes year of operation at Casper. Anon. *World Petrol.*, 1950, **21** (10), 56–9.—Description, with flow diagrams and section, of operation of Socony-Vacuum moving-bed T.C.C. unit on sour and sweet Wyoming crudes. Charge-stock inspections, operating conditions, and material balance are given. Alloy protection is employed where system exceeds 550° F and where temp might fall below dew point. Erosion combated by inserting metal dams where cat flow changes direction so that cat impinges on cat. E. B.

608. Seeligson natural gasoline plant world's largest in compressor horsepower. Anon. *World Petrol.*, 1950, **21** (8), 69–71.—Description of plant, including twelve Clark 1600-h.p. and two centrifugal 4200-h.p. compressors dealing with 98,000 million cu. ft/day producing 94,000 gal gasoline, 40,000 gal liq propane, 17,000 gal *iso*butane, 18,700 gal *n*-butane, 4000 gal kerosine, 1200 gal seal oil, and 1400 gal residuum. E. B.

609. Evaporation of liquids into turbulent gas streams. D. S. Maisel and T. K. Sherwood. *Chem. Engng Prog.*, 1950, **46** (3), 131–8.—Data are presented on the evaporation of liquids into turbulent gas streams from tests using wetted plane surfaces, cyl, spheres, and discs. Water was evaporated into air from each of the several shapes; water into CO_2 and into helium from cyl; benzene and carbon tetrachloride into air from cyl; and benzene into air from spheres. Values so obtained are expressed graphically as functions of the appropriate Reynolds Nos., and agree remarkably well with data from the literature. J. G. H.

610. Planning refinery heat transfer equipment. Part II. Efficiency and operating relations. T. G. Hicks. *Refiner*, 1950, **29** (10), 95–8.—(Cf. Abstract 391.) The series is continued with a consideration of the actual sizes of heat-exchangers. Algebraic relationships are tabulated for the various types of heat-exchangers under different conditions, making computation of necessary areas and ultimate temp a relatively simple operation. A brief discussion of optimum heat-exchange areas and pumping velocities and of standard types of construction is included.

Two illustrative examples on heat-exchangers are given. R. W. G.

611. Heat balance over cooling tower gives quick performance check. A. L. Hutchinson. *Petrol. Process.*, 1950, **5** (9), 953–7.—A method is presented for checking the performance of mechanical draught and atmospheric cooling towers in which the concept of theoretical trays is utilized. Individual tray and overall heat-balance relations are derived and examples evaluated. A tray-by-tray procedure is used to find the number of theoretical trays required and the water temp on each tray for given cooling conditions and a particular water-to-air-flow ratio. For use with the heat-balance relations a plot is given of total heat of dry air *versus* air wet-bulb temp. Results calculated for a mechanical draught tower under a particular set of conditions are illustrated graphically. A graphical method based on the heat balance is given for determining the theoretical tray requirements of atmospheric cooling towers, which differ from the former type in that the water makes multiple contact with fresh air, the air making only one contact with the water. D. W. F.

612. Tube-life charts. D. P. Thornton. *Petrol. Process.*, 1950, **5** (8), 827–9.—An illustration and description of use is given of a tube-life chart as prepared and used by the Phillips Petroleum Co. in connexion with maintenance of three gas-fired heaters in an ethylene plant, where frequent tube replacements are required. The chart basis is a curve, drawn up from a considerable amount of operational data on the performance of numerous tubes, representing average length of service to be expected from a particular tube in a given position. This aids in securing optimum service life of furnace tubes before replacement is necessary and enabling shut-downs to be planned instead of forced. D. W. F.

613. Safe, smokeless combustion features waste gas burner at Sinclair refinery. W. H. Decker. *Petrol. Process.*, 1950, **5** (9), 965–6.—A description with drawings is given of the waste-gas burner in use at the East Chicago refinery of the Sinclair Refining Co. The top of the 30-inch-dia gas stand-pipe is covered with a flat circular plate, supported a few inches above the pipe end from its periphery by a number of steel strips to form the burner. The head is enclosed by a cylindrical shroud, 5 ft 6 in in dia and 4 ft long, mounted on gussets. A high-pressure steam-ring with holes in the upper side is situated inside the shroud around the burner so that air for combustion is inspirated into the shroud past the burner head. Three pilot jets are mounted symmetrically around the stand-pipe enclosed by 4-inch guide pipes, the tops of which are flush with the bottom of the openings of the burner. Pre-ignition gas is supplied to each guide pipe, this being ignited by a spark ignitor. Each pilot jet is supplied from a separate gas line. D. W. F.

614. Removable insulation provided for refinery vessels. M. F. Allen. *Refiner*, 1950, **29** (10), 112–13.—Removable insulation necessary for vessels subject to high temp and stresses constructed of stainless-steel-clad carbon-steel plates for periodic inspection of welds. A procedure is described consisting of: (1) application of permanent insulation on the vessel plants; (2) application of removable insulation over weld-inspection lines; and (3) installation of sheet-metal jacketing. The insulation material employed is 85% magnesia applied with or without diatomaceous silica. Expansion of the insulation is allowed for by expansion joints. R. W. G.

615. One-man pipe alignment device. G. M. Wilson. *World Oil*, Oct. 1949, **129** (7), 198.—One end of a 5-ft length of 1-inch pipe is twisted in such a way that it will wrap in figure S fashion round slightly more than half the circumference of the pipe to be welded. Two short saddles of pipe of equal dia are welded on so that their open sides face each other. When placed in position the end saddle forms a cradle to support the other pipe until the welder has securely tacked the joint. A. H.

616. Ohio oil's flare stack igniters have " look-box " for safety in operation. Anon. *Petrol. Process.*, 1950, **5** (8), 851.—The flare-stack and ignition system in use at the Robinson, Ill., refinery of the Ohio Oil Co. is described. The flare tip consists of a 16-inch-dia, 18-8 s.s. pipe with a 5-ft-dia annular plate around the top as a flame guard, up through which pass three 1½-inch symmetrically-placed ignition pipes supplied from one line. Air and gas are fed to a look-box, made from a 1-inch high-pressure valve body, containing a sparking-plug, until an explosive mixture is formed continuously. The whole ignition pipe to the stack top is allowed to fill with this mixture, which is then exploded. The explosion flame travels up through the pipe from the look-box at the base and ignites the waste gas at the stack top. D. W. F.

617. Heat transfer. W. H. McAdams. *Chem. Engng Prog.*, 1950, **46** (3), 131.—The fundamentals of heat transfer are outlined, recent developments summarized, and fields for further work indicated. J. G. H.

618. Testing process instruments. O. G. Pamely-Evans. *Mech. World*, 19.1.51, **129** (3340), 58.—It is most important that instruments should be readily accessible for maintenance and testing. Wherever possible instruments relating to one process should be grouped on a single central panel. In this way any discrepancies in the indicated variables can be diagnosed immediately as either a process or instrument error. The paper deals with the testing of manometers, pressure gauges, temp indicators, flow meters, and differential meters. Ordinary U-tube liquid-filled manometers are not susceptible to error of indication if both limbs of the tube are read together. With single-limb readings, however, the instrument can be checked by means of a three-way cock in the pressure line leading to it. Pressure gauges can be checked by comparing them with a standard gauge. Temp indicators are best treated by the insertion of similar instruments into the process close to them. It is possible to buy thermometers with a National Physical Laboratory certificate of accuracy, and these can be used as standards to calibrate sub-standard instruments on process equipment. Methods of checking flow meters and differential meters are also described. A. S.

619. Concrete condenser box skims cooling water. Anon. *Oil Gas J.*, 7.12.50, **49** (31), 102.—Description of a condenser box 20 × 30 ft poured in three separate compartments and steel reinforced with dividing partition and outside walls 10 inches thick at top, to cool products of a solvent-refining unit. Flow is arranged through separate water-discharge boxes so that relatively clean water flows over the weir. G. A. C.

620. How five refiners organized their waste disposal programmes. J. S. Worden, W. B. Hart, J. S. Baum, W. E. Soden, and J. D. Tufts. *Petrol. Process.*, 1950, **5** (8), 836–7.—The methods and organization employed for pollution-control work at five refineries are described in a survey, as reported by representatives of these refineries. D. W. F.

621. Chart for best centre distance uses Vee-belt sheave ratio. F. H. Rumble. *Petrol. Process.*, 1950, **5** (8), 835.—A chart based on sheave ratios is given for use with V-belting problems to determine the shortest practicable or "ideal" centre-to-centre sheave distance. D. W. F.

622. Carbon in chemical engineering. W. S. Norman. *Birm. Univ. Chem. Engr*, 1950, **2**, 14–21.—The history of the use of carbon in the chemical industry is reviewed. The methods of manufacture of carbon and graphite are described, and the applications of these materials in chemical engineering are surveyed. The properties of carbon and graphite which are of value in the construction of chemical plant include resistance to most chemical reagents, including hydrofluoric acid and phosphoric acid at all temp, low coeff of thermal expansion, high resistance to thermal shock, high thermal and electrical conductivity, and ease of fabrication and assembly. D. F. J.

Distillation

623. Distillation column balance—overhead-bottoms split vs. the feed composition. W. D. Harbert. *Refiner*, 1950, **29** (10), 117–22.—Analogy is made between column balance and a weighing scale. Thus for a feed of 50 mol light component and 50 mol heavy component, the column will be in balance when it gives 50 mol overhead and 50 mol bottoms per 100 mol of feed. A shift away from this condition leads to marked deterioration of the purity of the increased product, with little difference in the reduced product, *e.g.*, for a constant degree of separation, increased overhead will necessitate greater proportion of heavy component in the distillate. Off-balance conditions thus affect calculated values of plant efficiencies, and the author believes that many of the irregularities in connexion with commercial column data are caused by this state. Suggestions for simple instrumentation, consisting of automatic control of reflux rate and feed preheat or two-point control of feed preheat, enabling balanced conditions to be maintained are given and discussed. The paper presents a comprehensive discussion of the question of balance, pointing out its difficulties and advantages. R. W. G.

624. Equilibrium flash calculator saves time and effort. W. A. Thomas, F. Fussman, and W. H. De Lany. *Petrol. Process.*, 1950, **5** (9), 948–9.—A special slide rule is described for solving multicomponent hydrocarbon equilibrium flash calculations, using the normal trial-and-error method. It is intended primarily as a time saver, but an accuracy of $\pm 1\%$ is also claimed. D. W. F.

625. The fugacity of propene and 1-butene. B. H. Sage and W. N. Lacy. *Refiner*, 1950, **29** (10), 123–7.—From experimental data on the vapour pressure and the influence of temp and pressure upon specific volume, the fugacities of propene and 1-butene have been determined for the liquid and gas phases at pressure up to 10,000 p.s.i. for temp ranges 40° to 340° F and 100° to 340° F respectively. From this data, values of equilibrium constants for pressures up to 800 p.s.i. were calculated. In addition to the above data being reported, values are compared with published data on the 1-butene–*n*-butane system, and the thermodynamic equations involving fugacity are given. R. W. G.

626. Multicomponent vapour–liquid equilibrium calculations made by punch-card system. J. W. Donnell and K. Turbin. *Refiner*, 1950, **29** (10), 109–11.—Illustrative procedure given for calculating bubble and dew points by means of punch-card machines, which are available in accounting departments of most refining companies. By preparing in advance a set of cards for different hydrocarbons with equilibrium values at different temp and pressures, equilibrium calculations may be made in approximately 5 min. Besides offering a material saving of time, the procedure is free from errors, and should be useful in the design and operation of distillation columns, condensers, reboilers, etc., in natural gasoline, general refining, and petrochemical plants, as well as in the study of composition change. R. W. G.

627. Thermal decomposition in lubricating oil distillation. K. K. Rumpf. *Erdöl u. Kohle*, 1950, **3**, 534–41.—Unfavourable dist conditions can cause marked deterioration

of lub oil distillates in respect of qualities such as colour and colour stability, pour point, ease of refining, visc, oxidn stability, etc. Examples are given. Relationship between cracking intensity and gas formation is discussed. Whilst dist temp is of importance for product deterioration, residence time in still is major factor at temp > approx 300° C; this is especially so in production of high-grade bitumen and cyl stock. V. B.

Absorption and Adsorption

628. Natural-gas processing. V. E. Middlebrook. *Oil Gas J.*, 7.12.50, **49** (31), 85.—A review of the history and résumé of current developments in natural-gas processing is given.

Many variations of highly complex oil-absorption units are available to-day, and flow sheets for five of them are given, and the processes discussed.

A sixth flow sheet for a combination absorption and re-absorption and rich-oil de-ethanization plant for 75% propane recovery is typical of plants under construction and to be built in near future. G. A. C.

629. On the differential equations of diffusion. J. D. Babbitt. *Canad. J. Res.*, 1950, **28A**, 449–74.—Following Muskat's development of the equation for the flow of a homogeneous fluid through porous media, the fundamental equations of diffusion are examined. The differential equations for interdiffusion of two gases, for the diffusion of vapours, and for the diffusion of gases and vapours through solids are derived from a dynamical equation defining the motion of the gas, an equation of continuity expressing the law of conservation of mass, and an equation of state giving the relation between concentration and pressure. For the diffusion of gases through absorbing solids, the dynamical equation of the flow is obtained by equating the space derivative of the spreading pressure of the adsorbed film to a resistive force equal to the product of the coefficient of resistance and the velocity of the film. The differential equations derived on this assumption agree qualitatively with measurements for the diffusion of gases through metals when the adsorption can be represented by Langmuir's equation. When adsorption follows the Brunaeuer, Emmett, and Teiller (B.E.T.) equation for polymolecular absorption, qualitative agreement is found with the diffusion of water vapour through hygroscopic materials. It is also shown that Fick's Law is not generally valid as the fundamental equation of diffusion. N. T.

Solvent Extraction and Dewaxing

630. Liquid–liquid equilibria of four-component systems. A. J. B. Cruickshank, N. Haertsh, and T. G. Hunter. *Industr. Engng. Chem.*, 1950, **42** (10), 2154–8.—A simple, rapid graphical method is presented for use with batch-extraction computations involving quaternary liquid systems. It is applicable only to systems in which three of the components are mutually miscible, the fourth being immiscible with one of the other three, and in which a straight-line quaternary equilibrium frustrum is exhibited. Many of the known systems of this type may be approximated to this. The method could possibly be adapted for curved profiles however.

The regular tetrahedron, with the four components as vertices, is orthogonally projected as a rectangle, so that length ratios on straight lines are correctly reproduced on the projection. The dia of the rectangle are taken as axes for plotting the equilibrium data on cartesian co-ordinates. The methods for locating a quaternary point and the resulting tie lines from the ternary data are clearly described. The results of a batch extraction of a binary mixture with a mixed solvent calculated by this and Hunter's previous method are compared with experimental results. The present method is considerably less time consuming. D. W. F.

Cracking

631. Conversion in Thermofor catalytic cracking. R. A. McKean and L. F. Grandey. *Chem. Engng Prog.*, 1950, **46** (5), 245–8.—An improved correlation of feed-stock conversion with space velocity and catalyst-to-oil ratio is presented, based on an empirical formula tested with pilot-plant and commercial data. J. G. H.

632. Catalytic cracking. Part III. M. Sittig. *Refiner*, 1950, **29** (10), 130–6.—(See Abstracts 2160, 2715—1950.)—Part III deals with the fluid cat cracking process, in which catalyst may average 300 mesh, whereas with the Thermofor process the range is 4 to 10 mesh. The paper outlines the history and development of the fluid process. Recent improvements mentioned include the use of micro-spheroidal catalyst giving lower attrition loss. Operation and mechanical features are also discussed. The paper includes a fairly extensive bibliography on the subject. R. W. G.

633. The Fawley cat cracker. F. J. Feeley. *I.P. Review*, 1950, **4**, 381.—The increased demand during the last fifteen years for better-quality motor-spirit has led to the need for a refinery process capable of producing greater yields of higher-octane material. Catalytic cracking, first introduced commercially in Louisiana in 1942, has assisted in fulfilling this need. This plant and a number of subsequent ones were all based upon the " up-flow " principle—the catalyst flowed upwards. In 1943–44 " down-flow " design was incorporated in plants erected by Standard Oil. The Fawley cat cracker is of the " down-flow " type, but incorporates many new features. Details of operation are given, together with a description of the following special features: structural steel supports, regenerator, reactor, large piping and expansion joints, slide valves, centrifugal air blowers and gas compressors, and built-in maintenance aids. R. H.

634. T.C.C. unit gives high liquid recovery by operating on vapour–liquid feed. W. C. Uhl. *Petrol. Process.*, 1950, **5** (9), 950–2.—As a result of certain design changes a conventional T.C.C. unit at the Casper, Wyo., refinery of Socony-Vacuum Oil Co. Inc., has been converted to operate on a combination feed of both vapour and liquid charge stocks, resulting in a higher liquid product recovery. A higher than normal catalyst-to-oil ratio of about 2·9 is used to supply the additional heat requirements, and circulation rate is about 100 tons/hr on 7500 b.d. total feed. The liquid portion of the reactor charge, amounting to about 23% of the total charge, consists of the entire bottoms from the cracking-furnace tar separator, and is introduced downwards into the catalyst bed as a fine cone-shaped spray inside the falling catalyst curtain. Results of a check run are given, including T.C.C. unit ultimate and component yields, operating conditions, and data on the liquid portion of the reactor charge. D. W. F.

635. The evaluation of converters for exothermic and endothermic catalytic reactions occurring within narrow temperature limits. G. Wirth. *U.S. Bur. Mines. Inf. Circ.*, 7587, Nov. 1950.—Basic calculations are developed for determining catalyst volumes of various types of reactors that give particular temp distributions. The types considered are: plate converters, inner-catalyst converters, outer-catalyst converters, and annular-vol converters. The four types are described and shown in diagrams, and each is considered theoretically. A diagram shows the direction of heat flow in the types of catalyst-filled cross-sections. With the help of the evolved formulæ, the individual types of construction are compared with regard to cooling surface and space utilization. To select a reactor of the proper size, it is necessary to consider still further other factors that do not appear in the calculations. For example, height of catalyst bed, linear gas capacity, ease of discharging, construction costs, and maintenance and operating costs. W. H. C.

636. Heat transfer in a fluidized solids bed. A. Baery, J. Klassen, and P. E. Gishler. *Canad. J. Res.*, 1950, **28F**, 287.—Experiments were performed to determine heat-transfer coefficients in a fluidized-solids bed under a variety of conditions. The variables studied were particle size, bulk density under non-fluidized conditions, and air velocity, but nothing has been investigated concerning variables such as bed temp, bed dimensions, and properties of the fluidizing gas. Simple correlations were established predicting the value of the heat-transfer coeff in the air-flow range investigated. An equation predicting the minimum fluidizing velocity was also derived. The heat-transfer coeff is almost unaffected by sp.ht. or specific conductivity. Chief application is the cracking of petroleum. A. D.

637. Heat and mass transfer in fluidized systems. K. N. Kettenring, E. L. Manderfield, and J. M. Smith. *Chem. Engng Prog.*, 1950, **46** (3), 139–45.—Rates of heat and mass transfer between the solid particles and the gas stream were measured for silica gel and activated alumina, fluidized in air. Data were obtained in a vacuum-jacketed glass tube 2·3 inches dia with particle ranges of 14 to 20, 20 to 28, 28 to 35, and 35 to 48 mesh with air mass velocity varying from 300 to 750 lb/(hr) (sq. ft.). Mean temp and partial pressure differences between the fluidized solid and gas stream were evaluated from thermocouple readings taken at intervals through the height of the bed.

Variations in void space and particle density were insufficient to establish the influence of these variables. The low values for heat- and mass-transfer coefficients obtained, in comparison with results for fixed beds, are in accordance with the fact that the particles tend to move with the gas in the fluidized condition. J. G. H.

638. Turbulent diffusion in fixed beds of packed solids. R. A. Bernard and R. H. Wilhelm. *Chem. Engng Prog.*, 1950, **46** (5), 233–44.—A study of turbulent diffusion in beds of packed solids through which a fluid is flowing. Liquid phase experiments were performed with a methylene-blue solution diffusing from a point source into water flowing through a bed of packed solids, and gas-phase experiments with carbon dioxide diffusing into an air stream in such a bed. Details are presented of the tubes and packings used in both liquid and gaseous experiments. Pressure-drop data were recorded and correlated, and applications of the results obtained are illustrated.

J. G. H.

639. Selection of cracking catalysts with aid of laboratory ageing. C. K. Viland. *Petrol. Process.*, 1950, **5** (8), 830–4.—A small laboratory fixed-bed catalytic cracking unit is described, and the procedure used in determining the ageing characteristics of catalysts with different feed stocks. The unit is a modification of one previously described in the literature (T. Rice and F. E. Ivey, *Proc. 27th Ann. Meeting A.P.I.*, 1947, **27** (3), 84–9). It is capable of fully automatic operation over a sufficiently long period of time to determine rates of decline in catalyst activity and changes in product distribution, 750 to 850 cracking cycles being usually adequate. Of the 50-min time cycle, 4 are for cracking and 15 for regeneration. The preheater and reactor are located in a 1¼-inch S.S. tube 3 ft long surrounded by a heat-transfer salt jacket maintained at 850° F. The catalyst temp during regeneration is restricted to 1100° F by the use of a special regeneration air distributor. Catalyst capacity is 200 ml of ¼ × ⅛-inch pellets, and the charge rate during the cracking period is 11·5 ml/min.

D. W. F.

Polymerization

640. The emulsion polymerization of isoprene. R. H. Clark, H. MacLean, N. Henderson, G. M. Barton, A. Johnson, J. T. Granlund, and W. L. Reynolds. *Canad. J. Res.*, 1950, **28F**, 351.—Initiation of polymerization of isoprene has been obtained with peroxide-peroxidase, various inorganic and organic catalysts such as dodecyl mercaptan, and ferrous sulphate, and it was also performed by air oxidation and anodic oxidation. Elastomers of polyisoprene were prepared with intrinsic visc from 1·5 to 4, with low gel content, and conversions up to 90% in 6 hr. The faster the conversion, the less tough is the elastomer. The physical properties of some of the elastomers have been measured, and these values are given. A. D.

641. Influence of pressure on the polymerization of styrene. R. C. Gillham. *Trans. Faraday Soc.*, 1950, **46**, 497–503.—Rate of styrene polymerization at 100° C increases 10-fold over pressure range 1 to 3000 atm and mol. wt. of polymer increases 1·55 times. Experimental details are given. Precautions were taken to obtain isothermal conditions; failure to do so considered to be cause of greater effects found by previous investigators. Results of experiments were confirmed by bulk polymerization in an emulsion using an emulsifying agent. E. B.

642. Copolymers of styrene and chloranil. J. W. Breitenback and A. J. Renner. *Canad. J. Res.*, 1950, **28B**, 507–14.—The copolymerization of styrene and chloranil in the presence of less than 1% of benzoyl peroxide. Reprecipitations of product showed

a chlorine content of 37 to 38·2%, corresponding to a copolymerization of mol. ratio of chloranil to styrene of 0·76 to 0·84. The molecular weights of the copolymer fractions were measured by an osmotic pressure method, in a micro modification of the Schulz and Hellige osmometer. Mol. wt. from 9000 to 30,000 were found, giving 21,000 for the original polymer. Copolymerization occurs with the carbonyl group of the chloranil being transformed into a derivative of tetra-chlorhydroquinone. This reaction has been verified by degradation of the copolymers with hydrogen bromide.

N. T.

Alkylation

643. Improved alkylation process. G. Weber. *Oil Gas J.*, 28.12.50, **49** (34), 78.—Principle points of improvement in the alkylation process include maintaining a high *iso*butane–olefin ratio in reaction zones, a higher overall acid concentration during reaction, improved contact of catalyst and feed stock, and incorporation of auto-refrigeration.

A flow chart of this new Kellogg process illustrates the article. G. A. C.

644. Synthesis of large ring dienes and their reaction with maleic anhydride. R. B. Ingraham, D. M. MacDonald, and K. Wiesner. *Canad. J. Res.*, Aug. 1950, **28B**, 453–9.—*cyclo*Tetradecen-one-3- was made by dehydration in the gas phase of *cyclo*tetradecanol-on-2. The former was the reduced with lithium aluminium hydride to *cyclo*tetradecan-ol-3, which was dehydrated to *cyclo*tetradecadiene. The maleic anhydride adduct was 3-6-decamethylene-tetrahydrophthallic anhydride. The same series of reactions was performed in the *cyclo*-octadecane series. N. T.

Chemical and Physical Refining

645. Continuous filtration—the influence of some variables on filtration rate and cake quality. H. Mondria. *Appl. Scientific Research, Holland*, 1950, **A2** (3), 165.—The introduction of relative quantities into continuous filtration equations eliminates constants relating to the nature of the slurry, so that the resulting equations present a general picture of the influence of different variables.

The influence of rotational speed of a rotary drum filter on its filtration rate is represented by a hyperbola, the shape of which is determined only by the ratio of cake to filter-cloth resistance at a definite reference rotational speed.

The extent to which the filter-cake is washed as a function of the rotation speed is demonstrated by means of simple equations. A method is given to deduce the variation of filter-cloth resistance with time from measurements of filtration rates. Other relations can be easily derived with the aid of the examples given. J. T.

646. Removal of hydrogen sulphide from industrial gases. R. M. Reed, C. Updegraff, and J. L. Parker. *Oil Gas J.*, 4.1.51, **49** (35), 48.—The importance of the hydrogen-sulphide removal from industrial gases and the various processes available are discussed.

Wet processes utilize a solution containing a reagent which combines with the hydrogen sulphide chemically to remove it from the gas stream. These include non-regenerative and regenerative processes. The only dry process in wide use employs iron oxide. Processes described include Seaboard, Girbotol, split-flow Girbotol, split-flow phosphate, and Thylox methods. Flow sheets are given.

Processes suited to selective removal of hydrogen sulphide in presence of carbon dioxide are included. G. A. C.

647. Skelly Oil successfully treats 600° E.P. distillate with cupric chloride slurry. Anon. *Oil Gas J.*, 14.12.50, **49** (32), 107.—The Perco slurry treating plant for sour gasoline at the El Dorado, Kansas, refinery is being used to process alternate charges of kerosine and 600° F E.P. distillate, using a copper slurry composed of Attapulgus clay, cupric chloride, and water.

Contact between distillate and reagent is made in the reactor, about 5500 b.d. being processed with about 688 lb slurry in circulation.

A flow sheet is given. G. A. C.

Special Processes

648. Gas-synthesis plant. Anon. *Petrol. Process.*, 1950, **5** (9), 946–7.—A brief description is given of the nearly completed Bureau of Mines gas-synthesis demonstration plant at Louisiana. A modified Fischer–Tropsch process is employed, the main differences from the German process being the use of a rugged iron catalyst and an internally oil-cooled " jiggling-bed " converter. The plant comprises five units: oxygen production, 98% at 1 ton/hr from a Linde Frankle unit; coal gasification in which any rank of coal is pulverized and gasified with oxygen and superheated steam, giving a gas consisting mainly of CO and H_2; gas purification, for the removal of sulphur compounds from the synthesis gas; hydrocarbon synthesis, for the catalytic conversion of the gases to liquid products and finally the product recovery and refining unit. Anticipated production is 55 to 60 b.d. 75-octane gasoline, 10 to 12 b.d. 80-octane diesel oil, and about 12 b.d. cracking stock. D. W. F.

649. Role of steam in the hydrogenation of carbon monoxide. (Reaction mechanism of the Fischer–Tropsch synthesis, pt. VI.) H. Kölbel and E. Engelhardt. *Erdöl u. Kohle*, 1950, **3**, 529–33.—In the Fischer–Tropsch synthesis using a Co cat main by-product is H_2O, whilst with a Fe cat it is CO_2, formed by a secondary reaction between CO and H_2O. Conversion of CO to CO_2 decreases with increasing space velocity; effect of latter and of temp on CO_2 formation is discussed. Excess of H_2O relative to CO can cause cat poisoning (by oxidn), Fe cat is more susceptible to this than Co. Latter can reduce CO at temp at which there is neither conversion of CO to CO_2 nor cat oxidn by H_2O. In case of Fe cat temp required to hydrogenate CO is such that cat will be attacked by H_2O unless sufficient excess CO is present. Effect of H_2O on cat was studied with N_2/H_2O mixtures. Oxidized cat cannot be regenerated by reducing gases (H_2, CO). Effect of operating duration on layer structure of cat was examined, in synthesis with Fe cat at normal space velocities with high H_2/CO ratios much of the cat is inactive. Work described was all carried out at atm pressure. Results obtained give theoretical justification for high space velocities, recycling, and use of fluidized cat recently introduced into processes utilizing Fe cat. V. B.

650. Synthetic liquid fuels—status of development in the U.S. H. A. Stiles. *Refiner*, 1950, **29** (10), 99–102.—A review of the present work on liquid fuel synthesis in the U.S. being directed by the Bureau of Mines. Coal to oil processing will be carried out in a plant capable of producing 300 to 400 b.d. of liquid fuel—products will include aviation gasoline base stock, motor gasoline, jet fuel, diesel fuel, and several grades of burner fuel at a cost only slightly higher than from petroleum. A Fischer–Tropsch or gas-synthesis plant operating on coal, with a capacity of 80 to 100 b.d. of liquid products, is due for completion in 1950. A shale-oil refining and treating unit of about 200 b.d. capacity has produced a variety of products for experimental purposes. Industry has put into operation some commercial units for gas synthesis, including the Hydrocol plant for converting either natural or coal gas into liquid products. The laboratory and pilot-plant data of the Bureau of Mines is expected to be of assistance to private industry in building commercial-scale plant. R. W. G.

Metering and Control

651. Atomic energy applied to measurement of catalyst level in cracking units. D. P. Thornton. *Petrol. Process.*, 1950, **5** (9), 941–5.—A level-indicating and control instrument, the Gagetron, and its application to the control of catalyst levels in catalytic-cracking plants is described. Its operation depends upon the transmission of γ radiation from a radium chloride source in a protected platinum casing through the catalyst bed, and the detection and counting by a Geiger counter tube. The intensity of radiation received by the counter is a function of catalyst-bed thickness only. Inside the catalyst hopper, several radium sources are located, all viewed by one counter outside the hopper, the location and amount of radium per source being so proportioned that no radiation from a particular source is detected by the counter when that source is covered by 2 ft of catalyst. The total radiation received is pre-

amplified at the hopper and fed to an integrating circuit, which is fed to the recording and control instrument. This output is directly proportional to the catalyst level in the hopper. D. W. F.

652. Emergency electrical power for refinery process control systems. J. M. Crothers. *Petrol. Process.*, 1950, **5** (9), 958–9.—A circuit is described incorporating a small (10 to 25 kW) steam-driven turbo-generator set, capable of supplying sufficient power for maintaining in operation during an emergency the essential control instruments of a refinery plant. The set is automatically brought in on the occurrence of a power failure to supply the necessary circuits, until the main emergency generator is in operation or normal power is resumed. D. W. F.

653. Flowmeter error in measuring pulsating flow. G. W. C. Tait. *Canad. J. Res.*, 1950, **28F**, 333.—Using variable-orifice flowmeters to measure air flow, discrepancies were obtained which could not be explained as due to the normal errors, such as faulty calibration, leaks in the system, etc. They were found to be due to the occurrence of rapid pulsations in the air flow. Theoretical analysis showed that the instruments were indicating root mean square rather than average flow rates. Experiments performed to test this were in reasonable agreement with the predicted values. Insertion of a suitable smoothing device between the pump and flowmeter minimized the errors. A. D.

654. Positive displacement meters for the measurement of petroleum products. J. D. Adams. *I.P. Review*, 1950, **47**, 358.—During recent years, considerable progress has been made in the design and application of positive displacement meters for the measurement of petroleum products. They fulfil a useful purpose in the petroleum industry, and if installed correctly they compare favourably in accuracy with other methods of oil measurement. As a general rule, accuracy in such meters can be judged by the repeatability of the results. One of the causes of inaccuracy is "slippage," which is more common with liquids of low viscosity than with those of higher. Details of calibration, design, and use of such meters are given. R. H.

PRODUCTS

Chemistry and Physics

655. On the adsorption of carbon monoxide on platinum catalyst. T. Kwan. *Bull. Chem. Soc. Japan*, Aug. 1950, **23** (3), 69.—From earlier work on the adsorption of hydrogen on reduced nickel, cobalt, and platinum, it was concluded by means of the statistical mechanical method that each of the metal atoms on the surface of the catalyst is equally capable of adsorbing a dissociated hydrogen atom. Extending the latter conclusion, it may be assumed that every metal atom at the catalyst surface behaves physically identically, even in the case of carbon monoxide adsorption. On the basis of this assumption the adsorbed state of carbon monoxide on platinum has been investigated, using the methods and procedures described. The results show that the assumption of adsorbed state $CO \rightleftarrows CO\ (a)$ fails to account for the experimental result, whereas the assumption of the dissociated state into $CO \rightleftarrows C\ (a) + O\ (a)$, gives the calculated values, which are somewhat in accord with the observed results. W. E. C.

656. Rate of hydrogen adsorption on reduced copper. T. Kwan. *Bull. Chem. Soc. Japan*, Aug. 1950, **25** (3), 73.—Secondary adsorption, poisoning, and incompleteness of reduction of copper metal catalysts are discussed. In the work reported special stress was placed on the complete reduction of the copper, with the result that contrary to the existing data an exceptionally large quantity of hydrogen was adsorbed with a rate proportional to the hydrogen pressure, without any slow stage taking place during the experiment. The procedure and materials used are described, and the observed

results are tabulated and discussed. The rate of hydrogen adsorption on two makes of copper, calculated according to the equation, $k = \frac{1}{t} \log \frac{P_0}{P}$, are :

Temp	Kojima's copper k mm Hg/hr	Khalbaum's copper k mm Hg/hr
300° C.	mean 0·00125	—
350° C.	,, 0·0056	mean 0·00447
400° C.	,, 0·020	,, 0·015

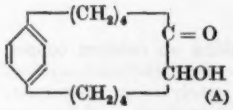
The heat of activation E, calculated from $E = RT^2 \frac{d \log k}{dT} = 20$ k.cal/mol. Inferences with respect to the adsorption equilibrium are given, and the heat of adsorption calculated according to the statistical mechanical expression, reported previously, is $\Delta\varepsilon > 35$ k.cal/mol. This value is far larger than any data so far reported, but is in accord with the 47 k.cal derived from spectroscopic data for the dissociation energy of CuH. W. H. C.

657. Application of the diene-synthesis to aromatic systems. G. Bruckner and J. Kovacs. *J. Hungarian Chem. Soc.*, 1949, **4**, 458–66.—Literature published in the last twenty years, after the report of Diels and Alder had been issued, has proved the general applicability of the diene-synthesis. Results of detailed investigations show that the diene-synthesis can be applied to mononuclear aromatic systems which possess unsaturated linkages located in side chains forming a conjugated system with the aromatic system. The diene-synthesis may suspend in certain cases the aromatic structure of these systems. The diene-synthesis strictly follows a stereo-selectivity, the principle of which consists in an " endo-*cis* " addition. H. T. A.

658. A system of process calculations for light hydrocarbons, Part I. A. J. L. Hutchinson. *Refiner*, 1950, **29** (10), 83–9.—The first of a series devoted to the simplification and standardization of calculation methods for light hydrocarbon processing plants. A fairly elementary and detailed review of the simple gas laws is given, including the ideal gas law and equilibrium behaviour. Reference is also made to the use of reduced temps and pressures in reporting gaseous conditions and to the PV–P relationships used in liquefication. R. W. G.

659. The purification of benzene. R. G. Evans, O. Ormrod, B. B. Goalby, and L. A. K. Staveley. *J. chem. Soc.*, Nov. 1950, 3346.—A method for the purification of benzene by the intermediate formation of the crystalline solid of formula $Ni(CN)_2,NH_3,C_6H_6$ obtained by shaking benzene with an ammoniacal solution of nickel cyanide is described. It is claimed that by this method benzene may be readily freed of saturated hydrocarbons that are difficult to remove by prolonged fractional crystallization or fractional distillation. J. H. P.

660. Synthesis of para-bridged benzene compounds. K. Wiesner, D. M. MacDonald, R. B. Ingraham, and R. B. Kelly. *Canad. J. Res.*, 1950, **28B**, 561.—Concluded that it should be possible to synthesize compounds with para-bridges containing less than 10 carbons from results which include : (1) the preparation of 2 : 5-tetradecamethylene and 2 : 5-decamethylene phthalic anhydride by dehydrogenation of corresponding tetrahydro compounds, and (2) ring closure giving a ten-membered para-bridged acyloin (A) in 70% yield.



(A)

The authors are at present attempting to synthesize the nine- and eight-membered bridges.

A. D.

661. Catalytic dehydrogenation of butane. J. Varga and M. Freund. *Hungarian J. Chem.*, 1950, **56**, 21–4.—Gaseous butane containing 0·5 vol per cent propane and 15·6 vol per cent *iso*butane was dehydrogenized at 560° to 580° C in the presence of chromium oxide catalyst precipitated on aluminium oxide. Product contained 29·6% hydrogen, 9·8% *iso*butane, 33·7% *n*-butane, and 20·9% butylene. H. T. A.

662. Communication concerning two papers presented at symposium on gas phase combustion. H. Muraour. *Rev. Inst. franç. Pétrole*, 1950, **5**, 148–52.—Discussion concerning papers covered by Abstracts Nos. 791 and 793, 1950.

663. Density, refractive index, boiling point, and vapour pressure of eight monoolefins (1-alkenes), six pentadiene, and two *cyclo*monoolefin hydrocarbons. A. F. Forziati, D. L. Camin, and F. D. Rossini. *Bur. Stand. J. Res., Wash.*, 1950, **45** (5), 406.—Density (at 20°, 25°, and 30° C), refractive index (at 6678, 6563, 5893, 5461, 5016, 4861, and 4358 Å, at 20°, 25°, and 30° C), vapour pressure, and b.p. (from 48 to 778 mm Hg) of sixteen highly purified hydrocarbons of the API-NBS series are reported for eight monolefins (1-alkene), six pentadiene, and two *cyclo*monoolefin hydrocarbons.

The data on refractive index were adjusted by means of modified Cauchy and Hartmann equations, and the values of the constants for each compound are given. Values are also given for the specific dispersions $(n_F - n_C)/d$ and $(n_g - N_D)/d$.

The data on v.p. were adjusted by the method of least squares and the three-constant Antoine equation. The value is given of the constants for each compound. J. T.

664. The effect of electrolytes on the strength of bentonite films. A. Buzach and E. Kugler. *J. Hungarian Chem. Soc.*, 1949, **4**, 466–72.—Strongly centrifuged suspensions of Transylvanian bentonite were poured on specially prepared surfaces: continuous, homogeneous, and flexible films were obtained. Effect of various electrolytes on the strength of these films was studied. Examined electrolytes can be divided into two groups: (1) NaCl, Na_2SO_4, MgCl, and $AlCl_3$; (2) NaCH, Na_2CO_3, and Na_3PO_4. Strength of the film was influenced by even slight concentration of electrolytes. Each of the curves showing the changes in the strength of the film has two maxima. In the first group of the electrolytes tested the first maximum was the higher. In the second group of electrolytes the second maximum was almost identical with the first or even slightly higher. Effect of electrolytes is correlated to the peptized, thixotropic, or coagulated condition of bentonite suspensions. Peptized suspensions provide bentonite films with the best mechanical properties: flexibility, elasticity, and high strength. Films of thixotropic gels were rigid and possessed less strength, continuous films could not be obtained from entirely coagulated suspensions. These changes can be explained by the actual changes in the cohesive forces between the bentonite particles.

H. T. A.

665. Experimental data on the viscous force exerted by a flowing fluid on a dense swarm of particles. H. Verschoor. *Appl. Scientific Research, Holland*, 1950, **A2** (2), 155.—Experimental data are presented to support Brinkman s modification of Darcy's law for fluid flow through porous media. The results of ten measurements performed are in close accordance with the prediction from theory. J. T.

666. Ferric soaps as catalysts for vinyl polymerization. J. N. Sen and S. R. Palit. *Nature*, 1950, **166**, 603.—The polymerization of styrene and methyl methacrylate is catalysed by purified ferric oleate, laurate, and stearate. It is found that: (1) the initial speed of polymerization is proportional to the nth power of monomer concentration ($3<n<4$), and rises rapidly with increase in catalyst concentration; (2) the degree of polymerization is proportional to $1/[\text{catalyst}]^{\frac{1}{2}}$, and to $1/[\text{monomer}]$; (3) the catalytic power under comparable experimental conditions is more prominent at lower temp, probably indicating a lower energy of activation for the catalysed reaction.

These features are in sharp contrast to the free-radical-type polymerization, although the polymerization of methyl methacrylate is inhibited by benzoquinone, characteristic of free radical polymerization. No reduction of the ferric soap is involved.

H. C. E.

667. The formation of crystalline complexes between urea and esters and their application to the separation of mixtures of esters. R. P. Linstead and M. Whalley. *J. chem. Soc.*, Nov. 1950, 2987.—The remarkable difference between hydrocarbons containing normal and branched chains in their power of forming complexes with urea is also met among carboxylic esters. A number of branched-chain esters failed to form crystalline complexes under conditions which yielded stable adducts from normal esters with a total chain length of about 10 atoms. Slightly shorter normal chains gave less stable complexes, and very simple esters none at all. The difference in properties has been used to separate mixtures of esters. J. H. P.

668. Heat effects in capillary flow. H. C. Brinkman. *Appl. Scientific Research, Holland*, 1950, **A2** (2), 120.—The temp distribution in a capillary due to energy dissipation of viscous flow is calculated while the heat conductivity of the fluid and the transport of heat by conduction are taken into consideration. J. T.

669. The influence of electric field on the convective heat transfer in liquids. G. Ahsmann and R. Kronig. *Appl. Scientific Research, Holland*, 1950, **A2** (3), 235.—It is shown experimentally that the convective heat transfer from a horizontal, electrically-heated wire to a concentric cylinder, filled with different non-conducting liquids is noticeably increased by the application of an electric field between the wire and the cylinder. The dependence of this effect on the nature of the liquid, the temp difference used, and the strength of the field is studied. A discussion is presented in terms of the similarity theory. J. T.

670. The rheological law underlying the Nutting equation. G. W. Scott Blair and M. Reiner. *Appl. Scientific Research, Holland*, 1950, **A2** (3), 225.—It is shown that by eliminating time from Nutting equation, $\psi = S^{\beta}\sigma^{-1}t^{k}$, this can be given a form in which both stress and strain may vary. This permits one to take account of pre-straining before the application of the stress.

For certain systems which do not obey the unmodified Nutting equation, the new law is found to be applicable, and the initial strain is related to stress by Bach's power law: $\sigma_0 \propto S^{k}$. J. T.

671. The mechanism of inhibition of the corrosion of iron by sodium hydroxide solutions. J. E. O. Mayne, J. W. Menter, and M. J. Pryor. *J. chem. Soc.*, Nov. 1950, p. 3229.—It is suggested that the film of γ-Fe_2O_3 formed on iron previously freed of its original air-formed film of oxide and immersed in 0·1*N*-sodium hydroxide containing dissolved oxygen is responsible for passivity, and results from a heterogeneous reaction between oxygen dissolved in the solution and the iron. J. H. P.

672. Microwave techniques for the measurement of the di-electric constant of fibres and films of high polymers. T. M. Shaw and J. J. Windle. *J. Appl. Phys.*, 1950, **21**, 956–61.—A resonant-cavity method is described for the determination of the dielectric constants, ε, of polymeric solids in the form of fibres, films, and thin cylinders. ε of polystyrene and polyethylene have been determined. The method appears to be accurate even when using small amounts of materials. D. F. J.

673. On the theory of extraction from falling droplets. R. Kronig and J. C. Brink. *Appl. Scientific Research, Holland*, 1950, **A2** (2), 142.—The extraction is investigated of a substance, dissolved in droplets of a fluid, when such droplets are rising or falling in another fluid under the influence of gravity. The circulation currents which are caused in the droplets by the viscous forces between the two fluids tend to modify the rate of extraction as compared with the case of droplets at rest. Under certain simplifying assumptions a differential equation is derived governing the combined action of convection and diffusion. The rate of extraction follows from the solution of an eigenvalue problem. J. T.

674. Parametric equations in the treatment of multicomponent systems. L. A. Dahl. *J. Phys. & Colloid Chem.*, 1950, **54**, 547–64.—The derivation and use of parametric equations in problems encountered in the investigation of phase equilibria are described. These problems are of two kinds: (1) the design of mixtures to be subjected to experi-

mental operations, and (2) the analytical interpretation of phase equilibria. When dealing with a system of a small number of components within a multicomponent system, parametric equations are relatively simple, and their form permits direct computation of the quantity of each component when values are assigned to the parameters. The operations required in deriving equations for estimating percentages of phases under specified conditions of equilibrium are simplified.

D. F. J.

675. The production, isolation, and purification of sulphur compounds, and measurement of their properties. A.P.I. Research Project 48A. *Ann. Rep. No.* 3, *U.S. Bur. Mines*, 1950.—This report covers the work accomplished during the year under Project 48A on sulphur compounds in petroleum and shale-oil products. The results are reported under three sections: synthesis, purification, and properties; thermodynamics; and separation and identification of the products obtained. The thermodynamics section records data on: low-temperature calorimetry, heats of combustion, vapour-heat capacities, and heats of vaporization; vapour pressures; and the calculated free-energy function, heat content, entropy, etc. Separation procedures are described covering preliminary distillation, adsorption, and fractionation, in which silica gel and "H-41" alumina were used. The alumina method gave the best results, as the concentrates obtained were comparatively free of aromatic compounds. Separation and identification by chemical means are described. The identification of six sulphur compounds from Wasson crude oil, by infra-red absorption spectrophotometry, and of methyl and ethyl mercaptans by mass spectrography is recorded. Twelve tables of data are given, and the infra-red spectra of fraction 35 and its components—1-propanethiol, 2-methyl-2-propanethiol, and 2-thiobutane—are shown. Appendices giving descriptions of standard samples and details of the separation by alumina are included.

W. H. C.

676. Properties of bentonite-sols and bentonite-gels. A. Buzagh. *Hungarian J. Chem.*, 1950, **56**, 7–10.—Extensive investigations have proved that bentonite is particularly suitable in colloidal chemistry as a model research material. Properties of bentonite are closely connected to the crystal structure of montmorillonite. Suspensions of montmorillonite and its sols behave as colloidal electrolytes. The abnormities of stability of bentonite suspensions can also be explained by the crystal structure of montmorillonite. Changes occurring in suspensions of bentonite under the effect of NaOH of increasing concentration are described in detail, and the theoretical explanation of the phenomena is given.

H. T. A.

677. Radio-active tracer study of an aliphatic acid in hydrocarbon oil. A. Gemant. *J. Phys. & Colloid Chem.*, 1950, **54**, 569–76.—The diffusion rate of C^{14} labelled tridecanoic acid in hydrocarbon oil was measured by allowing the radioactive solution of acid (0·005*N*) to diffuse into a fibre-glass mat holding the oil (visc 0·17 poise at 25° C) and measuring the increased count on a Geiger–Müller counter as solute diffuses into the solvent. Knowledge of the diffusion rate permits the investigation of a variety of problems.

Using Stokes' law to calculate the radius of the diffusing unit, tridecanoic acid was found to be molecularly dispersed in oil, the molecular radius being 2·5 Å. When an amine and a phenol were added, electrically conducting oils were produced, and the size of the units of the solute increased with the age of the solution. After two weeks the radius of the unit was 6·1 Å, and after four weeks, 8·4 Å. These radii correspond to associations of 4 and 11 mols respectively. The degree of adsorption of the acid by graphite and asphalt was determined, and the extent of the exchange reaction with copper acetate measured. When an oil containing the acid was oxidized at 150° C in Sligh oxidation flasks, a large fraction of the acid took part in the formation of polymer molecules, but, up to 200 hr oxidation, only to a small extent in the formation of solid precipitate.

D. F. J.

678. Reactions of organic peroxides. Part III. Oxidation of methyl*cyclo*pentane and methyl*cyclo*hexane. E. J. Casson, E. G. E. Hawkins, A. F. Millidge, and D. C. Quin. *J. chem. Soc.*, Oct. 1950, p. 2798.—Studies of the liquid-phase oxidation of methyl*cyclo*pentane and methyl*cyclo*hexane at 100° to 130° under pressure, showed that

alcohols, ketones, acids, and lactones are formed. These may arise from radicals produced from the hydroperoxides that result from limited initial oxidation of the hydrocarbons. J. H. P.

679. Reactions of organic peroxides. Part IV. Reactions of methyl*cyclo*pentyl and methyl*cyclo*hexyl hydroperoxides. E. G. E. Hawkins. *J. chem. Soc.*, Oct. 1950, p. 2801.—Continuing studies of the reaction of organic peroxides Part III (see Abstract No. 678) it has been shown that many of the decomposition products from methyl-*cyclo*pentyl and methyl*cyclo*hexyl hydroperoxide are similar to those formed during oxidation of methyl*cyclo*pentane. J. H. P.

680. Reactions of organic peroxides. Part V. Reaction of ferrous sulphate with methyl*cyclo*pentyl and methyl*cyclo*hexyl hydroperoxides. E. G. E. Hawkins and D. P. Young. *J. chem. Soc.*, Oct. 1950, p. 2804.—A continuation of work Part III and Part IV (see Abstracts Nos. 678–9). J. H. P.

681. The reactivity of β-naphthol and β-naphthylamines. F. Bell and W. H. Hunter. *J. chem. Soc.*, Oct. 1950, p. 2903.—Further evidence is presented to show the low reactivity of the 3-position in β-naphthols and β-naphthylamines. J. H. P.

682. Rheological changes during gel formation in adhesive systems. H. G. Higgins and K. F. Plomley. *Australian J. Appl. Sci.*, 1950, **1** (1), 1.—A method of obtaining experimental consistency curves for systems of rapidly changing rheological properties has been developed and has been used in the study of the gelation of various casein glues and synthetic resin adhesives. A rotating-cyl viscometer of Stormer type has been used throughout the experiments. J. T.

683. Studies of the viscosity and sedimentation of suspensions. Part I.—The viscosity of suspension of spherical particles. S. G. Ward and R. L. Whitmore. *Brit. J. Appl. Phys.*, 1950, **1**, 286.—The results are discussed of experiments carried out with systems of methyl–methacrylate spheres suspended in aqueous solutions. The relative visc in such systems is independent both of the visc of the suspending liquid and the absolute size of the spheres at a given concentration, but it is a function of their size distribution decreasing with increasing size range to a constant value. The constant of proportionality between specific visc and volume concentration at infinite dilution varies from about 4·0 for a size distribution of 1 : 1 to 1·9 for ratios exceeding 3 : 1. Dielectric particles in suspension in a non-polar liquid give rise to electrostatic charges which may affect the measurement of visc. J. T.

684. Studies of the viscosity and sedimentation of suspensions. Part 2.—The viscosity and sedimentation of suspensions of rough powders. S. G. Ward and R. L. Whitmore. *Brit. J. Appl. Phys.*, 1950, **1** (12), 325.—The visc of suspensions of rough methyl–methacrylate powders in aqueous solutions increases at all concentrations as the particle size is reduced. This is mainly due to liquid held in the irregularities of their surfaces which increase their effective vol. The thickness of this immobile liquid layer, for a particular material, is independent of the visc of the suspending liquid, the concentration of the suspension and the size of the particles above a certain min value below which it decreases continuously with particle size. Sedimentation experiments confirm these conclusions. J. T.

685. Suspending action of alkaline electrolytes on ilmenite black. R. C. Merrill and R. Getty. *J. Phys. & Colloid Chem.*, 1950, **54**, 489–97.—In addition to being of theoretical interest in the study of colloids, suspending action is important in paints, lubricating oils, printing inks, dry-cleaning solvents, and colloidal fuels. Suspending power was measured by shaking 200 ml of a 0·1% suspension of ilmenite black in a glass-stoppered 250-ml Pyrex glass cylinder for 1 min. After 3 hr standing at 23° C, a 50·0-ml sample was withdrawn through a stopcock attached at the 75-ml mark, and the sample analysed by measuring its light absorption in a photo-electric colorimeter.

Measurements of the suspending action on ilmenite black of solutions of sodium hydroxide, sodium carbonate, trisodium phosphate, sodium pyrophosphate, sodium

sesquisilicate, sodium metasilicate, $Na_2O.2{\cdot}98SiO_2$, and $Na_2O.3{\cdot}35SiO_2$ show max eff at low concn. Sodium dodecylbenzene sulphonate exhibits max eff at a higher concn. Mixtures of organic and inorganic detergents show two regions of max eff, probably due to each constituent, but the concn at which these occur are much lower than the corresponding concn for each one alone.

It is suggested that the mechanisms of suspending action involve separation of secondary aggregates into primary particles, decreasing the rate of sedimentation by electrostatic attraction between a charged particle and its ionic atmosphere, and increasing hydration or lyophilic nature of the particle surface. D. F. J.

686. The sorption of anionic detergents by wool. K. Swanston and R. C. Palmer. *J. Soc. Dyers and Colourists*, 1950, **66** (12), 632.—The rates of sorption of sodium cetyl sulphate by wool at 50° C at various salt concentrations have been measured; the results are explained qualitatively on the assumption that the ion concentrations have their stoichiometric relationship as in equilibrium systems. C. N. T.

687. Summarized Proceedings of a Conference on the Physics of Lubrication—Manchester, 1950. R. Schnurmann. *Brit. J. Appl. Phys.*, 1950, **1** (11), 275.—The papers and discussions summarized in this report fall under the two headings: (*a*) hydrodynamic lubrication and the rheology of lubricants and (*b*) boundary and extreme-pressure lubrication. J. T.

688. The reaction of diborane with some alkene oxides and vinyl compounds. F. G. A. Stone and H. J. Emeléus. *J. chem. Soc.*, Oct. 1950, p. 2755.—The effect was investigated of diborane on molecules where co-ordination might be followed by molecular re-arrangement, leading to further reaction, or where the transient existence of the borine molecule could initiate a reaction. Ethylene oxide and propylene oxide reacted readily with diborane at −80° C, forming diethoxyborine and a white polymeric solid and di*iso*propoxyborine and a liquid polymer respectively. It was shown that both polymers contained boron and were of the type $H{\cdot}(CHR{\cdot}CH_2O)_n{\cdot}BH_2$. The wax-like polymer from ethylene oxide had a melting range of from 45° to 50° and, like its analogue derived from propylene oxide, was hygroscopic, insoluble in ether, but soluble in water or alcohol with slight evolution of hydrogen. Both polymers depolymerized on heating *in vacuo*.

To correlate the reactivity of the borine molecule with that of boron trifluoride, ethylene oxide and boron trifluoride were reacted at −80° under the same conditions as for diborane. The reaction is highly exothermic, dioxan and an unstable liquid polymeric material being formed. It is suggested that in the reaction between boron trifluoride and ethylene oxide the latter itself acts as a co-catalyst. The reaction is also of interest in the study of boron trifluoride—catalysed polymerizations generally, as under normal conditions, any hydroxylic co-catalyst would be rigidly excluded. The presence of water vapour or other compounds containing a hydroxyl group has been known to be necessary for the polymerization of *iso*butene by boron trifluoride.

Preliminary experiments also were made to investigate the reactions of diborane with acrylonitrile, methyl methacrylate, and styrene. In each case the main product appeared to be a tri-alkyl boron derivative, but the reactions were shown to be complex, and are to be further investigated. J. H. P.

689. The reductive acetylation of aliphatic nitro-compounds. C. Simons. *J. chem. Soc.*, Sept. 1950, p. 2392.—The reductive acetylation of ethyl nitromalonate and ethyl nitrocyanoacetate to ethyl acetamidomalonate and acetamidocyanoacetate had been effected in 30% yield by zinc dust, acetic acid, and acetic anhydride. It is suggested that the low yield may be due to the ease with which the malonic ester, for example, enolizes on the carbon atom. J. H. P.

690. The synthesis of long-chain aliphatic acids from acetylenic compounds. Part IV: A new approach to the synthesis of branched-chain acids. C. L. Leese and R. A. Raphael. *J. chem. Soc.*, Oct. 1950, p. 2725.—The synthesis in good yields of monomethyl-substituted long-chain fatty acids from the easily accessible methyl ketones and acetylenic compounds is described. J. H. P.

691. Viscosity of liquids at high rates of shear. A. F. H. Ward, S. M. Neale, and N. F. Brilton. *Nature*, 1950, **166**, 905.—At high rates of shear it can be shown theoretically that ordinary lub oils have an anomalous visc which can be represented by the equation:

$$k \log \eta/\eta' = \frac{R\eta}{T^2} \cdot \frac{1}{1 + R\eta/11030T} = \phi(R, T)$$

where η and η' are the normal and anomalous viscosities at $T°$ K, R is the rate of shear (sec^{-1}), and k is a constant.

This equation is difficult to test because at high R, T tends to increase. The anomaly becomes less at high temp, and also η decreases with increased T. However, a plot of $\log \eta/\eta'$ against $\phi(R, T)$ of data for an S.A.E. 30 mineral oil in a high-speed rotational viscometer gives a straight line passing through the origin. H. C. E.

692. Viscosity-temperature dependence. A. V. Brancker. *Nature*, 1950, **166**, 905.—Neither of the equations $\log \eta = E/RT + \text{const}$ and $\log \log (\eta + c) = A \log T + B$, which are normally employed for expressing the variation of visc η with change in temp T, hold over a wide range of temp.

For water, many organic liquids, synthetic oils, bitumen, and molasses, the equation $\eta = a\eta/T + b$ has been found to apply over a wide temp range. Deviations appear at temp near the b.p.s of the liquids, but not at low temp where thixotropic effects have been reported. H. C. E.

Analysis and Testing

693. Absorptiometric colorimetry. C. H. Giles. *J. Soc. Dyers Colourists*, 1950, **66** (12), 615.—A review is given of the basic operating principles and construction of absorptiometric colorimeters. Other aspects considered are the Beer–Lambert Laws, photo-electric cells and colorimeters incorporating them, visual comparison instruments, apparatus for making continuous measurements, the reasons for the use of colour filters, and their correct selection, the determination of coloured substances in mixed solution, the accuracy of absorptiometric colorimeters, desirable future developments, and terminology. C. N. T.

694. Aerosol indicator for rapid testing of the dust content of air. G. Ljunggren and T. Wilner. *J. Chem. Met. and Mining Soc. S. Africa*, Oct. 1950, **51** (4), 171–3 (abstracted from *Tekn. Tidsk.*, 1950, **80** (23)).—An aerosol indicator is described, and is shown in a sectional diagram, which allows the direct determination of the dust content of air. The indicator operates in the same way as an ultra-microscope, and allows dust particles ranging down to $\frac{1}{2}$ μ to be observed. W. H. C.

695. Analogical computers. W. L. Morris and F. W. Bubb. *Petrol. Process.*, 1950, **5** (8), 838–40.—A computer adapted to the repeated solution of specialized process equations is the analogical type, the uses of which are described. The analogue computer, instead of operating with numbers, is concerned with physical quantities, each quantity in the relation to be analysed having its analogue in a specific quantity of the computer. It is used effectively in three types of problems:

(1) Those entailing lengthy trial-and-error methods, *e.g.*, flash vaporization of hydrocarbon mixtures;

(2) Those in which boundary and/or initial conditions are complex, *e.g.*, heat flow in irregularly shaped bodies with non-simple boundary conditions and fluid flow in petroleum reservoirs;

(3) Those in which attaining a rapid solution is essential to maintaining successful process operation.

The use of analogue computers as simulators for setting up a trial relation and comparing various solutions of this with a given relation is also discussed. Analogue computers are finding wide use for the integration of automatic control of processes. D. W. F.

696. The estimation of anionic detergents in solution by Hartley titrations. K. Swanston and R. C. Palmer. *J. Soc. Dyers and Colourists*, 1950, **66** (12), 630.—A quick, accurate, and straightforward modification of Hartley and Runnicles's method for estimating anionic detergents is given. No indicator is used, and an anionic or cationic detergent can be used in the burette. C. N. T.

697. An apparatus for the low temperature fractionation of small gas samples. D. J. Le Roy. *Canad. J. Res.*, Aug. 1950, **28B**, 492–500.—A simple apparatus has been developed for the fractionation of polycomponent gas samples at temps at which the take-off pressure is of the order of 0·5 mm. Fractions as small as 0·06 cc of gas have been isolated and their vapour pressure determined. N. T.

698. Apparatus for distillation on a semimicro scale. J. M. Conolly and G. Oldham. *Analyst*, 1951, **76**, 52. J. T.

699. End-point determinations sharply influenced by test variations. G. E. Mapstone. *Refiner*, 1950, **29** (10), 114–16.—The standard distillation methods A.S.T.M. D.86-46, A.S.T.M. D.216-40, and I.P. 123/49A for gasoline considered. By having the flask above the 1¼-inch hole in asbestos board, end-points are erroneously high, and repeatability is adversely affected. Increased size of flask gives reduced end-point values. It was found that, as long as the last 10% of the sample were distilled at the standard rate, the first 90% could be distilled as rapidly as the equipment would permit without significantly affecting the end-point. Non-standard apparatus was found unsuitable. R. W. G.

700. Multi-column molecular still has use in difficult hydrocarbon separations. Anon. *Petrol. Process.*, 1950, **5** (8), 857–8.—A multi-column, countercurrent molecular still developed by the National Bureau of Standards is described. Each column consists of a vertical central evaporating tube, 45 cm long and 2·5 cm O.D. over the surface of which the feed flows down in a thin film. This tube is surrounded by a concentric water-cooled condensing surface 4·1 cm I.D. The columns are arranged in line at successively higher levels, and are so connected that the residues flow from column to column in the downward direction, while the condensate is moved in the upward direction by magnetic pumps incorporated in receivers at the column base. Feed is pumped to the top of each column from a receiver into which flows condensate from the adjacent lower column and residue from the adjacent higher column. D. W. F.

701. Test mixtures for distillation at atmospheric and reduced pressure. C. B. Willingham and V. A. Sedlak. *Bur. Stand. J. Res., Wash.*, 1950, **45** (4), 315.—Values for the separation factor for distillation for each of the three pairs of diethylbenzenes in the pressure range 30 to 800 mm Hg are given. Data are also presented on the refractive index as a function of composition for the system 1 : 2-diethylbenzene and 1 : 3-diethylbenzene. J. T.

702. Composition of mineral oils in relation to their industrial uses. H. I. Waterman. *Bull. Technique Assoc. Ing. Bruxelles*, 1950, (4), 183–9.—Method (*n–d–M*) for analysis of mineral-oil structure has been developed and consists of formulæ (which are given) based on physical characteristics of thirty-four cuts (in the gas oil–lub oil range) obtained from five crudes of varying origins and of these cuts after progressive hydrogenation. Using these formulæ and knowing n, d, mean mol. wt., and S content, the following can be calc: % of C in total rings, aromatic rings, naphthenic rings, and paraffinic chains; No. of aromatic and naphthenic rings and total No. of rings. Two sets of formulæ are given, based on determination of n and d at 20° and 70° C. A simplified formula for calculating the total No. of rings (R_T) is:

$$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}=0{\cdot}3293+\frac{1{\cdot}536-1{\cdot}536R_T}{2{\cdot}660-1{\cdot}440R_T}\cdot(133-(n_a-n_c)\cdot 10^4);$$

except for high-mol.-wt. polycyclic mixtures, the error arising from the use of the

simplified expression is $\gtrsim 0{\cdot}2$ to $0{\cdot}3$ rings. Application of the method to hydrogenated lub oils (in which the H_2 content (as shown by sp. ref.) is related to V.I.) for predicting V.I. and to cracking of paraffin wax to follow course of reaction is illustrated.

V. B.

703. Determining the coke yield from mineral oils, tar pitch, and rough coal. B. Lanyi. *Aluminium (Hungary)*, 1949, **1**, 121–5.—Such determination processes consist essentially in pyrolytic decomposition followed by re-weighing the coke: the yield may be ascertained as percentage. A description is given of the methods of determination such as the Conradson and Ramsbottom processes, the "Bochum" test, as well as the Damian, Koetschau, Kelly, and Basset processes, used in different industries.

H. T. A.

704. Flash point determination. Anon. *Erdöl u. Kohle*, 1950, **3**, 565–6.—Draft Germans tandard (DIN 51758) for P.M.fl.pt. test (closed) for material flashing >65° C. Apparatus and procedure are essentially similar to I.P. 34/47. Flame is lowered into cup every 1° C; for referee tests mean of five determinations (within ±2° C of mean) is taken.

V. B.

705. A review of some developments in the use of the Karl Fischer reagent. A. G. Jones. *Analyst*, 1951, **76**, 5.—Recent developments in the use of the Karl Fischer reagent are reviewed under the headings of composition and preparation of the reagent, method of titration, and determination of the end-point and the versatility of the reagent. The relationship is examined between various theoretical and practical findings. The advantages and disadvantages of using the Fischer reagent in two solutions are discussed, and a few applications of the reagent mentioned. J. T.

706. Testing of gear oils with the four-ball oil tester. C. F. Krienke. *Erdöl u. Kohle*, 1950, **3**, 542–8.—Desirability of a test applicable to ordinary gear oils at a load level below seizure is discussed. Experiments were made using the four-ball tester at loadings of about 10 kg and $\gtrsim 50$ kg. Four oils (mineral, fatty, E.P., and a "hypoid gear oil") were examined, all of approx the same visc ($E_{50} = 18°$); test pieces were 12-mm-dia Cr steel balls. Wear was evaluated by microscopic measurement of wear area on ball surface. In all cases the hypoid oil showed the greatest wear, but the order of the remaining three oils varied with the test conditions, the fatty oil being better than the mineral at low loading and vice versa. It is stressed that oil behaviour at a given load cannot be used to predict behaviour at another load. Results of the present work do, however, agree with previously published findings regarding the behaviour of similar oils with actual gears.

V. B.

707. The nomogram in laboratory practice. C. G. Scott. *I.P. Review*, 1950, **4**, 387.—The nomogram is used extensively by the chemical engineer, but not to the same extent by the chemist. There is, however, a wide field of application by the chemist also. Simple nomograms can generally be constructed to cover the more common types of laboratory calculation, particularly those of a routine nature. The simplest type is the three-parallel-line type, where all the lines are on the logarithmic scale. The second type is used for the analysis of a ternary system, and is based upon circular scales. Details of the construction and application of these nomograms are given.

R. H.

708. A spectrophotometric determination of exhaust gas temperatures in the pulse-jet engine. J. F. Quinn. *Canad. J. Res.*, 1950, **28A**, 411–32.—The literature of the problem of temp measurement of non-luminous flames, *i.e.*, those which do not contain appreciable amounts of carbon in the form of soot, has been critically surveyed, and a review of the techniques used in the past fifty years is given. A method in which the flow of the gases is not impeded is necessary, and a spectrophotometric method, by which instantaneous values of a variable flame temp may be determined and continuously recorded, has been developed. This technique depends upon the attainment of monochromatic black-body radiation conditions in the flame for a small region of the visible spectrum, and the continuous measurement of radiation intensity in the above region, the radiation being correlated with the flame temp.

A description is given of the apparatus and the experimental techniques used by the author in the specific application of the method to the case of the time variation of the temp on the exhaust gases of a pulse jet engine. Details of the special type of spectrophotometer which employs a multiplier photocell as the radiation-detecting and measuring element and also a " black-body " cavity constructed as a standard radiation source for the calibration of the former instrument are included. The investigation of the emissivity of a flame coloured by alkali-metal vapours is described and its application to the present problem shown. The temp range over which the method is applicable and the inherent limitations of the new method are considered. N. T.

709. Turbulence in apparatus for measurement of streaming double refraction. H. G. Jerrard. *J. Appl. Phys.*, 1950, **21**, 1007–13.—The different apparatus used by thirty investigators who have induced double refraction in a liquid contained in the annular gap between two concentric cyl are examined with particular reference to the onset of turbulence. An explanation is given of the fact that with either the inner or outer cyl rotating, measurements of double refraction apparently show no sharp break between regions of laminar and turbulent flow. Advantages of using the outer cylinder as rotor are : (1) a larger gap can be used without the risk of turbulence, with consequent greater ease in optical measurements ; (2) with a larger gap the temp rise in the liquid is less ; (3) the instrument can be used as a Couette viscometer so that simultaneous measurements of double refraction and visc can be made ; (4) the onset of turbulence may be detected by irregularities in the torque-speed curve. D. F. J.

710. Thermodynamic properties of isotopic compounds of sulphur. A. P. Tudge and H. G. Thode. *Canad. J. Res.*, 1950, **28(B)**, 567.—The partition function ratios for many isotopic sulphur compounds have been calculated by means of statistical mechanics. From the values obtained equilibrium constants were determined for many possible exchange reactions involving the isotopes of sulphur. The results indicated that considerable fractionation of the sulphur isotopes can be expected in laboratory and naturally occurring processes. The authors discuss the predicted exchange constants in light of recent results on the distribution of the sulphur isotopes in nature. A. D.

711. History and theory of triaxial testing—1. V. A. Endersby. *Rds & Rd Constr.*, Feb. 1950, **28**, 50–4.—" Triaxial " is a form of mechanical test for road materials in which a load is applied axially to a cylindrical specimen of soil or bituminous mix, while a supporting pressure is maintained against its sides by air, water, glycerine, or other means, after which the stress-resistant properties of the material so tested are derived from the relation between the testing load and the lateral supporting pressure, cohesion, and angle of internal friction being deduced from Mohr's circle. Conventional methods of test for the plastic types of road materials are outlined, and the principles, development, and limitations of the triaxial test are described. J. G. H.

712. History and theory of triaxial testing—2. V. A. Endersby. *Rds & Rd Constr.*, Mar. 1950, **28**, 82–4.—The formation and development is outlined of Project Committee B-2 of the A.S.T.M., which later developed into the Triaxial Institute. Difficulties encountered in obtaining realistic test specimens are enumerated, and two types of machine constructed for this purpose described. Operating experience with these machines and conventional test equipment is compared. J. G. H.

713. Measurement of the heat output from radiant heating panels on a laboratory scale. F. Lipsett. *Canad. J. Res.*, 1950, **28F**, 257–79.—The amount of radiation from a miniature panel heating system was measured by means of a cubical variation of a standard heat meter, which was a 17-inch cubic box, particulars being given. Results show that radiation output of a large installation is equal to that found from the small panel. The heat transfer by convection was negligible. Adequate diagrams and photographs are appended. N. T.

714. Weathering tests on zinc oxide paints. J. R. Rischbieth. *J. Oil Col. Chem. Assoc.*, Nov. 1950, **33** (365), 471.—The differences in chalking properties of paints

containing zinc oxide of different manufacture were investigated in Australia. A brief account is given of the " First Exposure Trial." The " Second Exposure Trial " is discussed in detail in this article. Variables investigated were the pigmentation, the acid value of the linseed-oil vehicle, the proportion of bodied oil in a linseed-oil vehicle, and the time elapsing between the milling of the paint and its application. Results obtained are tabulated and discussed. Work reported elsewhere upon the superior resistance to checking and cracking exhibited by acicular and direct process zinc oxides has been supported by this present series of tests so far as they have progressed.

D. K.

715. Proposed tentative test methods for evaluation of continuous scouring of raw grease wool (AATCC Wool Scouring Committee). Anon. *Amer. Dyestuff Report*, 1950, **39** (24), p. 813.—A method is described for the laboratory evaluation of continuous wool scouring. It is adaptable to the comparison of detergents, builders, and other chemical factors in the scouring operation, and to the study of other variables. A standard apparatus and set of conditions are specified for calibration purposes, and may be varied to suit special needs. The criterion for scouring effectiveness is the extent of grease removal, and a rapid method of grease extraction is described.

C. N. T.

Crude Oil

716. Evaluation of crude petroleum. R. W. Grafton. *Birm. Univ. Chem. Engr*, 1950, **2**, 2–5.—The method of evaluation of a Venezuelan asphaltic crude oil is described, and uses of the evaluation data are indicated. D. F. J.

717. Refining properties of new crudes. Part 3. J. S. Ball, W. J. Wenger, and M. L. Whisman. *Petrol. Process.*, 1950, **5** (8), 842–6.—The results of analysis of twenty crude oils discovered in the Rocky Mountain region during 1948–49 are presented and compared as to characteristics and possible utilization with those of crudes from other fields in this area. Eleven of these crudes are from Wyoming, in which the Sussex area is the most active. Four are from Montana from the Bowes, Cut Bank, Sumatra, and Woman's Pocket fields, two from Colorado from the Dove Creek (condensate, San Juan Basin) and Oak Creek fields, two from the Ashley Valley and Roosevelt fields in the Uintah Basin of Utah, and one from outside the region in the Denver Basin of Nebraska. In general, the correlation index is comparatively low, the light fractions 4 to 7 averaging around 20 to 25 and the heavy fractions 13 to 15 around 30 to 55. Due to the paraffinic nature of the light fractions, these oils are unsuitable for manufacture of aviation base stock. Straight-run gasoline from these oils will be of low O.N., and may require sulphur removal. The production of suitable aliphatic solvents and a marketable kerosine appears feasible. The heavier fractions contain wax and are asphaltic in character, indicating low-grade diesel fuel and unsuitability for lub-oil manufacture, but from many of the oils a considerable amount of asphalt may be obtainable. D. W. F.

718. Refining properties of new crudes. Part 4—Crude oils from recent discoveries in Kansas. N. A. C. Smith, H. M. Smith, and C. M. McKinney. *Petrol. Process.*, 1950, **5** (9), 960–4.—Tabulated data are presented from analyses of fifteen Kansas crude oils from fields discovered during 1949. Of these, ten are from the Arbuckle formation, two from each of the Lansing group and Mississippi limestone, and one from the Viola limestone. All are of intermediate base, except the last, which is a paraffin-intermediate-base oil. Comparisons made via correlation-index curves with crude oils from two large Kansas fields show that, with the exception of the Viola oil, all are similar. Sulphur contents of crudes lie between 0·16 and 0·75%. A linear proportionality between carbon residue and sulphur content exists. In general, these oils yield a low O.N. straight-run gasoline, which is improved by cracking, etc., though unsuitable economically as base stock for aviation fuel. A good-quality high-gravity kerosine and high-cetane-number diesel fuel can be produced, though the presence of wax limits the max production of the latter. Only a little lubricating oil is obtainable.

D. W. F.

Gas

719. The calculation of pressure drop in a high pressure gas transmission system. A. H. van Gorcum. *Ingenieur*, **62** (49), W.113.—Formulæ are derived for the substitute resistance of parallel branches and for the equivalent load of small consumers.

For the actual computation of pressure drop, a special slide rule has been developed, and several constructions of this are proposed. The results obtained can be conveniently arranged in a diagram of the transmission system, giving a graphical representation of the flow in each pipe in addition to the pressures.

An electrical analogy of a gas-transmission network was constructed, in which the current was proportional to the gas stream and the potentials to the squares of the gas pressures. After adjusting the loads, the potentials in the various points of the system could be measured, thus enabling the pressures in the corresponding points to be found. R. R.

720. Chemical technology of natural gas. P. Benedek. *J. Hungarian Chem. Soc.*, 1949, **4**, 564–72.—Natural gas becomes ever more important as a raw material serving many branches of the organic-chemical industry. Methods of production of various hydrocarbons from natural gas are discussed in detail. Acetylene can be produced by electric arc, by pyrolysis, or by the oxidation process. The former is practical where electric current is cheap; the latter may be used at any place where natural-gas supply is inexpensive. Methods of concentration and refining of acetylene are considered. Six methods are described for the production of ethylene. The manufacture of propylene and of butylene is summarized. The technological description of compounds containing oxygen refers to detailed methods of production of formaldehyde ethylene oxide, ethylene glycol, ethyl alcohol, and other alcohols and glycerol. The so-called synthesis gas, which is produced from methane, serves as a basic material for the "Hydrocol" process. The cost of constructing a Hydrocol plant amounts to about 50% of the cost of a Fischer–Tropsch plant. H. T. A.

Engine Fuels

721. Application of equilibrium air distillation to gasoline performance calculations. E. M. Barber and J. H. Macpherson. *S.A.E. Trans.*, Jan. 1950, **4** (1), 15–23.—Equilibrium air distillation (EAD), the type of vaporization occurring when a liquid fuel, its vapour, and air are in equilibrium in an internal-combustion engine, can be used as data in dealing with problems of preparing combustible air–fuel-vapour mixtures from supplied air–liquid-fuel mixtures. EAD data also can be calculated from A.S.T.M distillation data. Details are presented of the apparatus and procedure employed in the direct measurement of EAD characteristics. Results so obtained with sixty-one fuels of widely differing characteristics in comparison with those obtained by calculation from A.S.T.M. distillation data showed an average deviation of 4·3° F, with a max of 12° F. It is concluded that this agreement is sufficiently close to enable the calculated data to be used for all practical purposes. The method of calculation from A.S.T.M. distillation data is outlined, and applications of EAD characteristics are indicated. J. G. H.

722. Effect of pressure on burning velocities of benzene–air, *n*-heptane–air, and 2 : 2 : 4-trimethylpentane–air mixtures. F. H. Garner, R. Long, and G. K. Ashforth. *Fuel*, Jan. 1951, **30** (1), 17–19.—Using the method described in a previous paper, a study has been made of the effects of pressure on the burning velocities of hydrocarbon–air mixtures at pressures of 400 to 700 mm Hg, using a burner 1·27 mm dia, the initial temp of the mixture being kept constant at 50° C. Shadow and direct photographs of the flames were taken and the evaluation of the burning velocities were made from the points of intersection of the curves obtained by plotting apparent burning velocity against r/R (r being the radius at which the apparent velocity is obtained from the relationship $V = U \sin \alpha$, and R the burner radius) for the shadow and luminous curves. In each case there is found to be an increase in burning velocity as the pressure is reduced. Graphs showing burning velocities of these mixtures plotted against pressure in atmospheres, using double logarithmetric scales, show that the results

satisfy a relationship of the form $V \propto p^n$. Similar data for 7 and 9% ethylene–air mixtures are given, and the values of n for each are tabulated for comparison with the value of −0·25 which would be obtained if the burning velocity varied inversely as the fourth root of the pressure. The observed data approx satisfy the inverse cube-root relationship. The mechanism of flame propagation is discussed. W. H. C.

723. The oxidation, decomposition, ignition and detonation of fuel vapours and gases. XVI. Benzene as a knocking fuel in conditions promoting the formation of finely divided carbon. R. O. King, E. J. Durand, and A. B. Allan. *Canad. J. Res.*, 1950, **28(F)**, 308.—Describes experiments which demonstrate that benzene becomes a knocking fuel when used in a spark-ignition Otto cycle engine if operating conditions are such that vapour–air mixture becomes impregnated with finely divided carbon. The flame of burning benzene impinged on relatively cool surfaces in the combustion chamber, and produced this carbon which was also formed by the burning of liquid drops dispersed in a combustible vapour–air mixture. The droplets were obtained by wet carburation, even when the overall mixture was weak; the engine being run with low-temp coolant, low-temp air supply, and with carburettor attached directly to the engine lead. It was evident from these experiments that the knocking combustion of benzene differs in some way from that of paraffinic fuels. A. D.

724. Influence of exhaust back pressure on antiknock performance of aviation fuels. W. E. Morris. *Refiner*, 1950, **29** (10), 92–4.—The fuel economy of reciprocating engines may be improved by compounding with gas turbines operating on exhaust. Influences of exhaust back pressure on anti-knock properties was studied using a supercharged C.F.R. engine with compression ratio of 7 : 1 and 8 : 1. Results show that the max rich mixture knock-limited power output of aviation gasoline is unaffected by increase in exhaust back pressure, although the corresponding fuel/air ratio is increased. The lean fuel/air conditions show appreciable decrease in power at increased exhaust back pressure, the decrease depending on the type of fuel and the C.R.—insensitive fuels such as *iso*-octane show less effect than conventional fuels, and less effect is noticed at the higher C.R. The adverse effects may be lessened by decreasing air-intake temp and by other design features. R. W. G.

725. Antiknock requirements of commercial vehicles. J. A. Edgar, H. J. Gibson, R. J. Greenshields, and G. W. Pusack. *S.A.E. Trans.*, Jan. 1950, **4** (1), 93–101.—The lack of data on the anti-knock requirements of commercial vehicles is remarked, and details are presented of a survey conducted during 1948 employing 102 commercial vehicles, using several different types of reference fuels and three commercial-type gasolines. The development and details of the test procedure used are outlined, together with the selection of test vehicles. From the data obtained it is concluded that while the fuel requirements of commercial-vehicle and passenger-car engines were found to be similar, on the basis of max requirement for knock-free operation, the commercial-vehicle engines have somewhat lower requirements at high speeds, and tend to rate sensitive fuels slightly lower at high speeds than do passenger-car engines at the same speeds. Attention to ignition-system components will reduce the large variation in anti-knock requirements frequently encountered among engines of the same make and model. Engine severity is discussed, and is found to be not necessarily associated with engine size. J. G. H.

726. Jet fuels—What kind at what cost? Anon. *Petrol. Process.*, 1950, **5** (8), 824–6. (*From a report by A. R. Ogston.*)—The question of the most practical type of fuel for use in aircraft gas-turbine engines is discussed. For passenger airlines fuels of the general characteristics of kerosine come closest to satisfying the needs of max safety combined with max combustion efficiency, fuel economy, and freedom from corrosion and deposit-forming characteristics. Due to its higher flash point a higher standard of safety is attainable by using kerosine. The use of normal-burning kerosine, the fuel generally used at present, greatly simplifies supply and distribution. As airline demand increases it may prove desirable to establish a separate grade, as all the characteristics of domestic kerosine are not required. U.S. armed services specifications are given, together with those proposed for commercial airline turbine fuels, based on the British ecification D.Eng.D.R. 3482. It is considered that for commercial use a max f.p.

specification of −40° C, as in England, is preferable to −60° C max f.p. of the U.S. specifications, as the former requirement can be met with out great difficulty. Also for the immediate future it should be possible to supply kerosine-type turbo fuel at 4 to 5 c/gal below the present airport cost of Grade 100/130 gasoline. D. W. F.

727. Combustion in diesel engines. H. Ricardo. *Gas Oil Pwr*, 1950, **45**, 267–9.—When an oil droplet is introduced into air at a temp above its ignition point a short time elapses before the shell of vapour ignites. The flame is then fed by evaporation from the liquid core of the droplet, and burns at a rate controlled by the O_2 supply until all the oil is consumed. This is the mechanism by which fuel burns in a C.I. engine.

In a diesel engine combustion occurs in three stages : a delay period before ignition commences ; a period of rapid pressure rise during ignition of the main bulk of the fuel ; and a period during which the remainder of the fuel burns as it enters the combustion chamber. The pressure in stage 2 depends upon the extent of the delay in stage 1, and for smooth running this delay must be small. But if there were no delay the droplets would not be dispersed and slow burning would result. Since the delay is less at high temp, which can be caused by faster running, it is possible to keep the delay period constant in terms of crank-angle degrees.

The droplet size must not be reduced below a certain minimum because : (1) it must have sufficient momentum to carry it through the surrounding atmosphere, and (2) the greater the number of individual droplets the greater the uncontrolled pressure rise of stage 2. Thus the lower the injection pressure becomes, the larger are the fuel droplets and the smoother the running.

The delay period depends upon : (1) the droplet size, (2) the volatility of the fuel, and (3) the C.N. of the fuel.

The temp of the combustion-chamber air can be raised by : (1) preheating ; (2) increasing the C.R. ; (3) inserting a heat-insulated member into the combustion chamber. There are objections to (1) and (2), and provided that the member is not in the incoming air stream (3) is the best method ; since : (*a*) it does not reduce the density of the air by preheating, (*b*) it serves to keep the delay period constant in terms of crank angle, and (*c*) its high temp eliminates carbon or ash deposits.

The amount of air swirl necessary depends on the number of injector holes, and in, for example, a four-stroke sleeve-valve engine it is possible to create an adequate swirl even for a single-hole injector. With poppet valves multi-hole injectors are required. Compression swirl does not provide a complete solution to this problem, for with its use the fuel consumed is 10 to 15% more than in an engine employing direct injection and induction swirl.

The shape of the combustion chamber and the number and direction of the fuel jets all contribute to the degree of fuel combustion, and in practice the optimum conditions must be found by trial and error. H. C. E.

728. 1950 diesel-fuel survey. O. C. Blade. *Oil Gas J.*, 28.12.50, **49** (34), 81.—A summary of analyses is given of 266 samples of diesel fuel manufactured by fifty-six companies. The fuels are classified by types of service (bus, tractors, railroad, etc.) and A.S.T.M. grades 1, 2, and 4D. G. A. C.

729. National Annual Diesel Fuel Survey, 1950. O. C. Blade. *U.S. Bur. Mines Rep. Invest.* 4746, Nov. 1950.—This survey records the results of fourteen laboratory tests and determinations on 266 samples of fuels made by fifty-six companies on their products manufactured during the year. The data are given under two classifications : (1) according to the A.S.T.M. grades, 1-D ; 2-D having pour points of 0° C and below ; 2-D, having pour points above 0° C, and 4-D. (2) According to service, viz., diesel fuels : (i) for bus and similar operation ; (ii) for trucks and tractors, etc. ; (iii) for railroad work ; (iv) for stationary and marine engines. Included in the analyses are some data concerning the A.S.T.M. grade of burner fuel oil, under which designation the fuel is also marketed. W. H. C.

730. Oil and gas fuel mixture reduces operating costs. G. M. Wilson. *World Oil*, Nov. 1949, **129** (8), 220.—In an attempt to attain higher h.p. from two 150-h.p. engines driving two 5 × 24-inch duplex pumps, experiments were conducted in which a

measured amount of dry fuel gas was injected and mixed with the oil then being used as fuel. One-quarter natural gas and three-quarter fuel-oil mixture greatly improved engine-power output, and resulted in cleaner fuel-injection nozzles, valves, and rings. Max discharge pressures could be raised from 700 to 900 p.s.i. Fuel oil consumption was decreased from 300 brl/month to about 190 brl. A. H.

731. Residual oil utilization. O. W. Willcox. *World Petrol.*, 1950, **21** (10), 72, 74.—Principle of Texaco engine discussed and illustrated. Introduction of Texaco-type engines and manufacture of high B.Th.U. gas from heavy fuel oil would reduce gas, coke, and unworkable heavy residues from crude oil from 21 to 4%, thus moving refiner's output into higher price brackets. E. B.

732. Inflammation of methyl and ethyl nitrate vapours. Characteristics of the explosion process and intermediate reactions involving nitrogen dioxide. P. Gray and A. D. Yoffe. *J. chem. Soc.*, Nov. 1950, p. 3180.—The pressure limit of spontaneous ignition (explosion limit) of methyl nitrate vapour was found to be dependent on the nature of the containing-vessel surface and to be lowered to different extents by different inert gases. Explosion was aided more by argon than by carbon dioxide. In discussing the mechanism of the different modes of decomposition of methyl and ethyl nitrates, the authors suggest that the explosion of the alkyl nitrates be assigned to the class of ignitions called " chain-thermal." J. H. P.

Lubricants

733. Alloyed oils. R. D. Streeton and A. C. Mauchan. *I.P. Review*, 1950, **47**, 349.—The incorporation of additives in lubricants dates back to about 1850, prior to the use of petroleum oils. From then onwards, various additives were employed for different purposes, and special methods of refining petroleum lurbicants were introduced. During the 1930s and 1940s the issue of patents upon additives increased considerably. At present, the following additives are used : (1) pour-point depressants—these reduce the amount of dewaxing necessary on the plant, and allow improved qualities in other respects due to the presence of wax ; (2) V.I. improvers—improve the cold-starting characteristics and oil consumption ; (3) E.P. additives—enable the lubricant to withstand high-pressure gears like hypoids ; (4) oxidation inhibitors—overcome excessive corrosion due to hotter-running engines and the use of metallic alloys ; (5) detergents—prevent ring-sticking. Thus research into the use of additives costs a lot, but eases the work of the refinery, and also reduces the significance of the nature of the crude. Work on synthetic lubricants has been in progress for a number of years. R. H.

734. Compressor lubrication. K. L. Hollister. *Lubr. Engng.*, Aug. 1950, **6** (4), 158–60.—A suggested procedure for the study of compressor lubrication comprises determination of the properties of the various oils, examination of the requirements of the different types of compressors, and the selection, from the foregoing data, of the best oil for each type of compressor. Five commercial oils are discussed, properties considered including wear factors, water reaction, carbon formation, and low-temp characteristics. Single- and two-stage air compressors, high-pressure, and diesel-engine compressors are considered in some detail. J. G. H.

735. Fundamentals of cutting fluid action. M. E. Merchant. *Lubr. Engng.*, Aug. 1950, **6** (4), 163–7, 181.—The basic functions of cutting fluids are outlined. Cooling action and the mechanism and benefits of friction reduction are discussed, together with chip formation, and the relationships between cooling properties, cutting speed, and friction reduction are considered. J. G. H.

736. The action of cutting oils. Anon. *Mech. World*, 19.1.51, **129** (3440), 52.—A number of photographs are presented showing exactly where a cutting lubricant is to be applied to improve the surface finish of the work. These photographs were taken in the Shell Research Laboratories, and the indication is that the lubricant is effective only when it penetrates the tool-clearance crevice. The experimental work was carried out on a milling machine used as a planer and a single-edged tool arranged to take a

full-width cut on a 1-inch-wide specimen. A syringe was used to apply drops of oil during the formation of different types of chip.

Photographs show the effect on the surface finish of: (*a*) a single drop of oil; (*b*) flooding the clearance crevice with oil half-way along the cut; and (*c*) flooding the rake crevice. A. S.

737. Lubrication of diesel engines. H. J. Nicholson. *Gas Oil Pwr*, 1950, **45**, 280.—Lubrication of cyl of C.I. engines presents difficulties because of: (1) high temp and pressures; (2) thrust due to angularity of connecting-rod (with trunk pistons); (3) close contact of the oil with O_2 at high temp during the compression stroke. Deposits are often due to bad combustion of the fuel or to dirty induction air, and not to the lub oil.

Lubrication of bearings is accomplished by the circulation of large quantities of oil through the engine. The use of telescopic pipes for conveying cooling oil to and from pistons promotes aeration, which is undesirable. Usual contaminants found in the crankcase are: combustion soot, which arrives as a result of blow-by; unburnt fuel oil; iron oxide from piping, etc.; salt or fresh water from leaking cooling systems. Solids can be removed by regular filtration, but fuel oil cannot be removed at any ordinary plant.

Deterioration of the oil may be caused by excessive pressures, which reduces the oil volume at the bearing surfaces and produces conditions suitable for rapid oil oxidation. H. C. E.

738. High-additive oils rated in " gas " engine service. Anon. *Petrol. Process.*, 1950, **5** (8), 846–50.—A brief review with excerpts is given of the papers and discussion at the A.S.T.M. symposium on high-additive content oils, San Francisco, Oct. 12, 1949, together with some of the data from field tests on the new oils in gasoline engines. The new-type oils considered are known as Supplemental 1 and 2 and Series 2 oils, and differ from the previous heavy-duty engine oils in that they contain from five to ten times as much additive. D. W. F.

739. Selection, care, installation of antifriction bearings. J. A. Trail. *Oil Gas J.*, 7.12.50, **49** (31), 94.—Points in connexion with proper care of bearings include avoidance of dirty surroundings, removal of all dirt from housings, handling bearings with clean hands or clean canvas gloves, use of clean solvents (avoiding leaded gasolines), and storage of bearings in oilproof paper when not in use.

In selection of bearings for machinery, experience is a great factor; and where expected loads are known, bearings based on a weighted average load calculated from the root mean cube of the various loads and the length of time these loads are to be encountered, can be selected.

Examples are given and solutions provided in four different cases.

Various types of installations are discussed; for example, where two opposed dual-purpose bearings can be used to support a shaft; or maintenance of endwise location in either direction by each of two opposing bearings.

Special conditions require close co-ordination between customer and bearing manufacturer. G. A. C.

740. Pumping characteristics of an 180-degree journal bearing. A. E. Roach. *Lubr. Engng.*, June 1950, **6** (3), 122–5.—While the ability of a journal bearing to function as a pump when a hole is drilled through it into the high-pressure oil film has been recognized for a considerable period, little attention has been paid to this phenomena. In view of the possibility of such a function being of especial value under particular conditions, an investigation was undertaken as to how far a journal bearing could be effective in this direction without adverse effect on primary load-conveying functions. The essential data relating to the development of oil-film pressure in journal bearings are briefly reviewed and the apparatus and method of operation employed in the investigation described. The results obtained indicate that while a journal bearing can be operated as a pump without detriment to its primary function, a large safety factor is necessary and performance is not of such a character as would lead to the selection of a bearing pump where this was the only duty imposed on the unit; the natural field of application would be rather in those special situations where pumping service could be imposed as a secondary duty. J. G. H.

741. Studies of the load-carrying capacity of sleeve bearings. C. M. Allen and K. A. Davis. *Lubr. Engng.*, Aug. 1950, **6** (4), 161–2.—During the course of a fundamental study of sleeve bearings, bearing tests were run on such materials as copper, brass, constantan, and Invar, as well as on conventional bearing materials. The excellence of the results obtained with the unconventional bearing metals led to the running of further tests simulating imperfections known to exist in service. Under these conditions copper still performed better than either babbit or copper–lead. If normal practice is sound, these results would indicate the absence in the test of some significant factor in bearing performance. The apparatus and procedures employed are described and possible explanations indicated. J. G. H.

742. The lubrication engineer. His establishment and development in industry. G. D. Jordan. *Lubr. Engng.*, Aug. 1950, **6** (4), 168–70.—The development of the idea of the lubrication engineer in industry is outlined, and the necessary qualifications are discussed together with education and propaganda, bulk storage of lubricants, testing, prevention of waste, reclamation, and lubricating systems. J. G. H.

743. Lubricants for precision instruments. P. Csokan. *J. Hungarian Chem. Soc.*, 1949, **4**, 336–43.—The theory of lubricating precision instruments and the physicochemical characteristics of lubricants are discussed. A method was evolved and a refining device designed for the production of lubricating oils similar to the Cuypers' type oils (for watches and precision instruments). One of the products is equivalent to Cuypers' oil No. 1 possessing the following characteristics: visc., 86·5 cs, solidification point, −20° C; neutralization number, 0·05: volatile ingredients, 0·05%; water, 0·03%. Oil equivalent to Cuypers' No. 2 can also be easily produced, and further investigations are in progress to determine the conditions for preparing oils identical to Cuypers' oils No. 3, 4, and 5 and to find suitable anti-oxidants. H. T. A.

744. Why turbo-alternator oil deteriorates. Anon. *Mech. World*, 22.12.50, **128** (3336), 584.—For many years it has been the aim of oil suppliers to produce a turbine oil which will lubricate efficiently at all working temp without deterioration, which will be suitable for any make or size of turbine, and will have an economical life. The deterioration of the oil is due to chemical action by oxidation, aeration, and over-heating. The entrance of steam and water to the oil system and formation of water–oil emulsions, the corrosion of the metals in the system and the interaction of oil-oxidation products with the corrosion products to form metallic soaps are factors. Oil which has deteriorated rapidly forms sludge which impairs oil circulation and heat transfer. The passage of an electrical current through oil causes the oil to become very dark in colour, and in some cases results in a deposit of a fairly hard nature. The current is sometimes due to an unbalanced magnetic field which causes an induced current to be set up in the shaft of the machine. When selecting an oil the following three items require close attention: (*a*) anticipated life; (*b*) initial cost; (*c*) the amount of make-up oil required.

Some turbine manufacturers recommend that to obtain good results and to prevent the accumulation of sludge and water a small quantity of oil should be drawn off periodically and replaced by fresh oil. A. S.

745. Viscosity–temperature dependence of lubricating oils. A. V. Brancker. *Scientific Lubrication*, Oct. 1950, **2** (10), 22–3.—The fundamental visc–temp equation is stated, and its limitations with reference to the effect of additives on oil viscosities are noted. A modified equation is developed which gives a linear relationship between n/T and $1/T$ over a range of temp extending from 60° C to −38° C for Avtol oil and 100° C to −10° C for water. J. G. H.

746. Oil reclaiming symposium. D. M. Cleaveland *et al.* *Lubr. Engng*, Oct. 1950, **6** (5), 208–18.—Reclamation of industrial petroleum products; reclaiming of used lubricating oil; reclaiming industrial petroleum products; centrifugal reclamation of industrial petroleum products; reclaiming petroleum products by filtration; aviation lubricating oil re-refining practice; reclamation of crankcase lubrication oil for railroad diesel locomotives; oil-filtration insurance; re-refining of used mineral oils by treatment with activated clay and heat. J. G. H.

747. General grease characteristics versus bearing requirements. T. G. Roehner. *Lubr. Engng.*, Oct. 1950, **6** (5), 220–4.—The problem of lubrication of bearings by grease is approached by defining bearing requirements in terms of grease characteristics which will satisfy these demands. Methods of application are considered in some detail, particularly with respect to separability tendencies, and contributory factors are enumerated. The effects of such bearing operating conditions as temp, speed, and load on lubrication requirements are discussed, together with frequency of application and the effect of contaminants, particularly water. The significance of bearing design as a factor in the amount of grease fed to the moving bearing surfaces is outlined, and the temp variations experienced with fully packed ball bearings during the initial running period are explained. J. G. H.

748. Energizable lubricant. Anon. *World Oil*, Oct. 1949, **129** (7), 201–3.—A grease-type lubricant, which has the ability to store energy during compression and to utilize this energy for a gradual continuous feeding of the lubricant sliding surfaces, has been developed for pressurized plug valves by Nordstorm Valve Division, Rockwell Manufacturing Company. Frequency of lubrication by the normal method should be considerably reduced. It is expected that such a " compressible " fluid will have applications in other fields. A. H.

Bitumen, Asphalt, and Tar

749. Automatic binder batcher for an asphalt plant. W. L. Russell. *Rds & Rd Constr.*, June 1950, **28**, 178–80.—The significance of the proportion of binder in bituminous surfacing compositions is stressed, and the need for reliable automatic methods of proportioning emphasized. Details are presented of a small semi-automatic device designed at the Road Research Laboratory for batching bituminous binders by vol, intended for use with the laboratory's small asphalt plant mixing 2-cwt batches which will deliver any required quantity of binder up to about 5¼ gal. Operating procedure and results are included. J. G. H.

750. Plant stability test for hot-mix asphaltic concrete mixtures. T. Y. Chu and M. G. Spangler. *Rds & Streets*, Oct. 1950, **93** (10), 83.—A new method of control testing of asphaltic concrete mixtures which is speedy to operate, is described. It involves the use of a versatile cylindrical mould in which the specimen is prepared and tested. A dia/height (D/H) ratio of unity is at present used. Stability and deformation results are determined during the application of a vertical load in the direction of the cylindrical axis. Details of compaction and operation, and of the interpretation of results are given, but the work is still only in the initial stages. R. H.

751. Rubberized asphalt surfacings : experimental work in Singapore. Anon. *Rds & Rd Constr.*, Aug. 1950, **28**, 247–9.—Details are presented of experimental rubber asphalt surfacing carried out in Singapore in May 1950. Four sections of a main traffic route were selected for treatment, and details of the mixtures and procedures employed are given, together with the laboratory tests used. J. G. H.

752. Some aspects of bituminous roads in America. A. R .Lee. *Rds & Rd Constr.*, Aug. 1950, **28**, 253–4.—The features of bituminous surfaces on American roads are noted, and the function of the Federal Bureau of Public Works is outlined. Factors contributing to the high standard of American roads are summarized, and the subjects under investigation by road authorities are enumerated. J. G. H.

753. Some aspects of skidding in relation to the non-skid properties of asphaltic road surfaces, tyre and vehicle design. C. Greville-Smith. *Rds & Rd Constr.*, May 1950, **28**, 140–3 ; June 1950, **28**, 168–72.—The factors which promote skidding are enumerated and vehicle design and tyre design discussed. Asphalt road surface design and texture are considered in detail from the standpoint of initial design and retention of non-skid properties. Methods of rendering existing slipping surfaces non-skid are detailed, and the measurement of slipperiness from the road surface and tyre aspect is discussed, together with the measurement of other related road-surface characteristics. J. G. H.

Special Hydrocarbon Products

754. Grinding fluids. L. H. Sudholz, S. Manilych, and G. S. Mapes. *Mech. Engng*, Dec. 1950, **72**, 963.—The efficiency of a grinding wheel decreases as the wheel face becomes dull, this dulling being caused by abrasive points wearing down to flats or by loading of the grinding wheel. The loading may be either gum or metallic loading, the former occurring when the grinding fluid deposits a gummy material on the surface of the wheel. This difficulty can usually be eliminated by correct use of a suitable grinding fluid. Metallic loading is such that pores of the wheel pack become filled with metal particles, leaving no space for chip clearance. The paper is concerned with the latter type of loading. Test equipment and a test procedure are described by which recording and measuring of the degree of metallic wheel loading can be carried out.

Two types of metal were used in the investigation, and the results are given of metallic wheel-loading evaluation obtained with several different types of cutting fluids. It was found that heavy duty soluble oil was superior to all the other grinding fluids, including the non-petroleum type on both metals.

Future work is in progress to confirm the relationship between power and consumption and wheel wear and the degree of metallic loading. A. S.

755. Metal-working oils. G. Cibula. *Erdöl u. Kohle*, 1950, **3**, 569–73.—A general discussion on desirable properties of such oils and the various uses therefor; pH should usually be 7 to 10 to assist anti-rust action. A distinction is made between "drilling oils" ("Bohröle") used in dilution (down to 1%) as an emulsion with water and "cutting oils" ("Schneidöle"), which contain E.P. additives and are not emulsified. Both these types of oil are used in processes involving cutting. Other shaping processes for metals (pressing, rolling, wire-drawing, etc.) where temp is lower, rarely exceeding 250° C, can frequently utilize lubricants such as straight or compounded mineral oils, fatty oils, or graphite; although drilling and cutting oils also find frequent application in this field. V. B.

756. Paraffin and microcrystalline waxes. D. T. Jones. *Soap*, Nov. 1950, **26** (11), 125.—Crystalline-type wax consists principally of saturated straight-chain hydrocarbons ranging from C_{17} to C_{60}, with small amounts of unsaturated material which is probably responsible for its darkening on exposure to air.

To determine the quality of wax, tensile-strength measurements are frequently used, since it has been established that the wax containing the larger crystals has the lower tensile strength.

It has been found that a small amount of microcrystalline wax in paraffin of a plate or needle type will induce a malcrystalline type of structure.

Microcrystalline waxes are generally prepared by solvent extraction of petroleum slack wax, using methyl ethyl ketone, and their colour can be improved by clay treatment. They are distinguished from paraffin waxes by their indistinct crystal structure, their high retentivity for oil, and their high tensile strength. They can now be produced in more ductile form by incorporating in them a moderate amount of definite crystalline type of material of low melting point. This does not affect the high-melting-point property of the original micro wax.

Paraffin waxes will not take up oil readily but have high retentivity for solvents, a property which is of particular importance in the formulation of wax polishes.

It appears that microcrystalline waxes contain natural inhibitors of a dark, relatively unstable, resin type which will impart a malcrystalline structure to paraffin wax.

The possibility of making blends of micro, paraffin, and polyethylene resin is a great advance, since the resin will impart high gloss. However, such blends suffer from the draw-back of being difficult to emulsify. Ability of a polish to give good gloss can be judged by refractive index, but, when applying such a test, it must be borne in mind that a high oil content will give high refractive index but very poor gloss. O. M.

Coal, Shale, and Peat

757. Production of wax from Hungarian brown coal. T. Valatin. *J. Hungarian Chem. Soc.*, 1949, **4**, 510–12.—Results of the investigation of various types of Hungarian brown coal are discussed. Coal samples were treated with benzene or a mixture

of benzene–alcohol. The bitumen obtained by this extraction was further separated by means of various solvents. A sample of Dorog brown coal showed the highest content of bitumen (9·0%). This bitumen consisted of 22 to 28% resin, 22 to 25% wax, and 40 to 45% pitch. The practical advantage of Dorog coal is that its mixture content averages only 12 to 13%; therefore, it does not require any dehydrating treatment. The Hungarian wax obtained by these extraction methods consists chiefly of free esters. It seems especially well suited for industrial purposes, where ceric acids of high melting points are needed. Its solvent-resorbing capacity is poor, however, in relation to turpentine. It appears that the resin and pitch obtained as by-products are also suitable for various industrial purposes. H. T. A.

758. A thermal decomposition study of Colorado oil shale. A. B. Hubbard and W. E. Robinson. *U.S. Bur. Mines Rep Invest.* 4744, Nov. 1950.—An investigation is reported of the specific reaction rates for the thermal breakdown of the kerogen in Colorado oil shale at temp from 350° to 525° C. The oil shales used assayed 26·5, 52·6, and 74·0 gal oil/ton, by the modified Fischer retort method. Characteristics of the sample, kerogen content of the raw shale, apparatus and reagents used are described. The kerogen content of the samples—based on: (1) the modified Fischer assay; (2) ashing the shale, conversion of the kerogen in the samples to gas, oil, and bitumen, time–temp rate of decomposition—is given. Decomposition rate and decomposition products were the same for all samples under the same conditions. W. H. C.

Miscellaneous Products

759. Production of floor polishes. L. R. Sadler. *Chem. Prod.*, Dec. 1950, **13** (13), 491.—The advent of harder waxes, such as Carnauba, and the call for floor polishes that give a better finish and that can be more easily applied, has led to the following basic formula being developed for such products: carnauba wax (5 to 20%), which imparts a high gloss; beeswax (10 to 30%), which acts as a binder between solvent and hard wax; ceresine (25 to 35%) which prevents the formation of "carnauba rings" by modifying crystal structure; paraffin wax (40 to 70%), which acts as a wax diluent and softening agent; solvent (2–4 :1), usually white spirit, to render the polish easy to apply; perfume (Q.s.) in the form of nitrobenzene or synthetic floral odorant.

This basic formula is subject to modification through considerations of cost, type of climate, and season for which the polish is required, etc. The latter requirement is often met by the introduction of a gelling agent such as aluminium stearate.

Methods of testing polishes involve determination of melting point, colour, hardness, and wax/solvent ratio. O. M.

760. Absorption spectroscopy in paint research—a survey. N. H. E. Ahlers. *J. Oil Col. Chem. Assoc.*, Oct. 1950, **33** (364), 421.—Absorption in the ultra-violet and infra-red regions is discussed, the actual wavelengths used being 200 to 350 μ in the ultra-violet and 2·5 to 25 μ in the infra-red. A brief account of the theory underlying absorption spectroscopy in the two regions is presented. Typical forms of ultra-violet spectrophotometer and infra-red instrument are described, together with the techniques to be employed. The applications of ultra-violet spectroscopy are essentially analytical and diagnostic in nature. They include: estimation of purity and determination of impurities; determination of conjugation arising from a reaction; alkali isomerization for the production of conjugated systems; recording the spectra of oils for identification purposes; analysis of rosin acids; transmission measurements and analysis for trace metals. The applications of infra-red spectroscopy are also frequently analytical in nature, but the scope of analysis which they offer is wider than for ultra-violet spectroscopy. They include: finger-printing; structural determinations; following changes of structure during the course of reaction, and analytical techniques. The ultra-violet and infra-red spectra of various substances are included. There are forty-three literature references. D. K.

761. Petroleum solvents. F. Preu. *Official Digest*, 1950 (309), 745–9.—Petroleum solvents used in the paint and varnish industry are reviewed and discussed. J. T.

762. Rosin as an insecticide adhesive. J. A. Jenson, W. T. Lumerford, and R. W. Fay. *Soap*, Nov. 1950, **261** (11), 121.—Public knowledge of the disease-carrying capabilities of flies has led to a demand for community control of these pests by spraying of their breeding grounds out of doors.

The residual effect of chlorinated insecticides, such as D.D.T., when applied in emulsified systems indoors, is reasonable, but this does not hold good when such formulations are subjected to rain. Therefore, a laboratory investigation was put in hand to develop an emulsion spray containing a builder which would meet requirements for residual effect under any conditions.

This work has led to the establishment of the following satisfactory formula for an emulsifiable concentrate: D.D.T., 25%; xylene, 63%; suitable emulsifier, 2%; pine gum rosin, 10%, in which the builder is the pine gum rosin. O. M.

Corrosion

763. Notes on galvanic corrosion. F. L. Laque and W. D. Mogerman. *World Oil*, Oct. 1949, **129** (7), 153–4.—The theory of galvanic (or bi-metallic) corrosion is given. The galvanic series of metals and alloys is presented, together with hints on avoiding or minimizing this type of corrosion, *e.g.*, by selection of material and by avoiding combinations where the area of the less noble material is relatively small. A. H.

764. Some electrical relations in galvanic couples. H. D. Holler. *Bur. Stand. J. Res., Wash.*, 1950, **45** (5), 373.—The electrical relations for a galvanic couple with and without polarization by externally applied current are developed and their significance in the derivation of criteria for cathodic protection is demonstrated. J. T.

765. Some aspects of the protection of iron and steel against corrosion. U. R. Evans. *J. Oil Col. Chem. Assoc.*, Oct. 1950, **33** (364), 452.—Superficial oxidation of iron and steel in air is rapid at high temp, at ordinary temp oxidation is detectable but soon becomes very slow. However, iron in contact with water rusts, due to the formation of ferric hydroxide some distance from the metal. This, owing to its position of formation, has no protective action, and the reaction does not stifle itself. Presence of certain salts in the water speeds up the attack, and it is of an electrochemical character. If either anodic or cathodic products are sparingly soluble, attack of this nature is usually prevented. Strongly adsorbable substances such as lead soaps can also prevent attack by water. It is thought that metallic lead paints may solve the problem of providing a paint with reasonable keeping and good anti-corrosive properties. Anti-corrosive paint must be applied to clean metal. Scale and rust can be removed by pickling, grinding, or grit blasting. Another promising type of primer is a paint richly pigmented with metallic zinc. The vehicle may be polystyrene, chlororubber, basic zinc chloride, or zinc phosphate. There are fifteen literature references. D. K.

766. Influence of different types of formation waters on disintegration of cements. R. C. Clark. *Petrol. Tech.*, Aug. 1950, **2** (8), 9–10.—Small cylinders of twenty samples of set cement were placed in various corrosive waters in the laboratory for nine months. Most of the cement slurries were made with tap water, but a few were mixed with sulphate water. In field tests the specimens were put in a screen-wire thimble in the gas anchors of insert pumps in wells in six different fields. Resistance was determined by the condition of the samples and the number of samples of each that were in good condition at the end of each immersion period. It was found that, in general, the cements with less than 5% of tricalcium aluminate were most resistant to corrosion. The waters were also placed in order of corrosiveness.

In practice, corrosion will not be as rapid as in these tests unless a channel develops through which formation waters can flow. Sulphate and sulphide waters cause most corrosion. G. D. H.

767. Application of wear-resistant phosphate coatings to ferrous surfaces. M. B. Roosa. *Lubr. Engng.*, June 1950, **6** (3), 117–21.—Details are given of a process, using a bath of metal acid phosphates containing free phosphoric acid and an accelerating

agent, for the deposition of phosphates of manganese and iron on ferrous components for automotive assembly. Advantages claimed include prevention of welding of metals under load, increased lubrication efficiency resulting from the formation of an absorptive crystalline coating, carrying evenly-distributed minute oil reservoirs, rapid break-in and chemical removal of irregularities remaining after machining operations. The preliminary and subsequent cleaning and rinsing operations are enumerated and variations available in the crystalline structure, according to the functions of the components so treated and the tolerances called for, are outlined. J. G. H.

768. Plastic tubing in salt water disposal well. A. Gibbon. *World Oil*, Nov. 1949, **129** (8), 151–4.—A recent successful installation of a complete string of 3387 ft of all plastic tubing is indicative of the extent to which light-weight low-tensile materials may be utilized. The basic material, Carlon " B," is a special grade of cellulose acetate butyrate. In general, it is immune from the effects of dilute acids, alkalis, fresh and brine waters, corrosive soil conditions, and organics (with the general exception of chlorinated solvents and aromatics). The extra heavy plastic tubing has the added mechanical features of upset male and female adapters and standard length threads that permit its being handled with standard tools (slips, elevators, and chain tongs). Tables show the physical properties of Carlon " B " and the wt, dia, and burst pressures of standard pipe and tubing. A. H.

769. Protective coatings for offshore rigs. L. R. Whiting. *World Oil*, Nov. 1949, **129** (8), 110–12.—The vinyl resins have proved most successful coatings for combating corrosion by sulphur compounds, seawater, weather, etc. Although more expensive, sand blasting is highly recommended for surface preparation. The wash primer adheres strongly to steel, stainless steel, Zn, Cd, Cu, Ni, Cr, anodized Al, galvanized steel, and Mg. This is followed by anti-corrosive and anti-fouling coats. For use in seawater the paint system is based on vinyl chloride–acetate resins coupled with one of the vinyl butyral resins. A. H.

770. Protecting machine parts from corrosion. Anon. *Mech. World*, 19.1.51, **129** (3340), 49.—Most corrosion preventatives function by providing a water-resistant barrier and by forming on the metal a layer of naturally-occurring or specially-added inhibitors. The most commonly occurring materials can be divided into soft-film, hard-film, and oil-film types, the soft film being further divided in solvent deposited, hot-dip, smearing, and slushing types. Solvent-deposited films are usually lanolin or petrolatum mixtures dispersed in a solvent such as white spirit. Soft films applied by hot dipping are based on petrolatum. Smearing materials for cold application are usually lubricating greases. Hard films contain plasticized resins or bitumens, and the solvents are petrol-like or carbon tetrachloride or trichlorethelyne types. For slow drying white spirit or coal-tar naphtha can be used. Oil fluid films are not so preventative as solid films, but have a definite use on internal surfaces where solid material could not be tolerated. A number of other temporary corrosion preventatives are described, and the causes of their failure classified. Methods of applying the above preventatives are given. A. S.

771. First electric-welded high-pressure vessels ever fabricated. Complete 25 years of refining service. Anon. *Oil Gas J.*, 14.12.50, **49** (32), 101.—In 1925 the Texas Co. installed at its Port Arthur refinery twenty-four vessels in four new Holmes–Manley cracking units, thus adapting thermal cracking to successful commercial operation by use of strong ductile welds. Some of these vessels are still in service. G. A. C.

Engines and Automotive Equipment

772. Compound engine systems for aircraft. E. J. Maganiells, L. V. Humble, and D. S. Boman. *S.A.E. Trans.*, Jan. 1950, **4** (1), 79–92.—Previous work on the utilization of exhaust-gas energy of aircraft engines to increase engine power and economy is noted and a comparison presented of the performance of engine systems having different types and degrees of compounding, together with the load-range characteristics of aircraft powered with these systems. The systems of exhaust-gas turbines

generally used are described with performance data, and special points discussed include the effect of back pressure on component power, net power, and fuel consumption, and the effect of altitude, compression ratio, and improved fuel. The special advantages to be gained from the spark-ignition compound engine are outlined, and the longer development period necessary for this type of compounding is emphasized.
J. G. H.

773. Modern methods of testing aero-engines and power plants. A. C. Lovesay. *J. Roy. Aero. Soc.*, 1950, **54**, 327.—Some of the more interesting present-day test methods for the gas-turbine engine are described. They fall into three categories: (1) component-testing; (2) performance and functional investigation; (3) engine endurance. It is concluded from the work described that there are four aims for future development: (1) fuller instrumentation for bench engines in the early stages; (2) co-ordination of rigs (*e.g.*, combustion-type) with engine conditions; (3) wider distribution of testing on rigs; (4) flight-testing for establishing or confirming engine performance at altitude.
C. N. T.

774. Post-war development of the reciprocating engine. F. J. Wilgard and E. H. Olson. *S.A.E. Trans.*, Jan. 1950, **4** (1), 8–14, 23.—During the past ten years the development of the C18 (Wright) aviation engine has resulted in an increase in h.p. output of 60% and a weight reduction of 40% with improved operating economy and greater dependability. The methods employed to attain this end are described, and include the incorporation of a forged-head cyl with improved cooling performance, improved valve-seat durability, modifications in piston and piston-ring design and materials, crankcase improvements, and the incorporation of a low-voltage ignition system.
J. G. H.

775. The high speed light weight diesel engine. J. H. D. Middleton. *Trans. Inst. mar. Engrs*, Dec. 1950, **62** (12), 353.—For the past twenty-five years the diesel-engine designer has been endeavouring to challenge the petrol engine for aircraft application. The chief advantage of the diesel engine is its greater economy, but on the other hand it is considerably heavier due to its most robust construction. Other advantages are simplicity in construction, elimination of vital electrical auxiliaries, use of fuel of lower volatility and greater reliability. Early diesel engines used in aircraft were the Beardmore and the Mercedes Benz. Eventually, however, the diesel engine for aircraft was discarded when it became clear that it could not compete with the petrol engine for military purposes. At the same time the same type of light-weight diesel gradually proved itself to be most useful in light naval craft. The paper describes and illustrates the General Motors model 16–184A (the "Pancake"); the Mercedes Benz type MB 511; the Junkers Jumo 205E; the Paxman Ricardo Ex 239A, and the Perkins T.12. Comparisons are made between the various design features of the above engines, and it is suggested that there is a need for an engine of about 2000 b.h.p. with a specific weight of 3·5 lb/b.h.p. A large number of detailed drawings are included, together with photographs of engines and engine parts, and performance curves.
A. S.

776. How the sleeve valve could improve the diesel. Anon. *Mech. World*, 12.1.51, **129** (3339), 29.—Sir Harry Ricardo recalls the outstanding features of twelve years of research into the behaviour and functions of the single sleeve valve. As the result of the findings in an aero-engine development programme, the application of the sleeve valve to high-speed diesel engines was also investigated and found to reveal advantages with respect to thermal efficiency and durability. The first batch of engines made as a result of this work have behaved well and maintained their extremely low fuel consumption for more than twenty years. They have also shown in many cases negligible wear after running over 60,000 hr. Early experiments indicated that real future for this type of engine lay in the propulsion of heavy road vehicles. Bench and road tests on such vehicles showed excellent results. Because of the prejudice against double sleeves, manufacturers refused to adopt the single sleeve which had been developed. An attempt was therefore made to apply the knowledge gained in the above research programme to poppet valves. Eventually a poppet valve was developed which had great success. Nevertheless, the advantages of the single sleeve valve remain, and

these are listed. It is stated the best application of the sleeve-valve engine is in the really large engine working for very long hours and at high load factors. The low rate of wear and the very low oil consumption would in these applications show up to best advantage. A. S.

777. Floating diesel-electric power plant. Anon. *Gas Oil Pwr*, 1950, **45**, 313–16.—The power for a 1200-kW diesel-electric floating cutter-dredger, of capacity 1300 cu. yd. sand per hr, is provided by five Caterpillar Vee-form four-stroke engines, each with twelve cyl of dimensions $5\frac{3}{4}$-inch bore and 8-inch stroke. Each engine has an output of 407 b.h.p. at 1200 r.p.m., corresponding to a b.m.e.p. of 106 p.s.i., and has a C.R. of 16 : 1. Pressure-charging is by means of a Roots-type blower driven from the crankshaft.

The engines are cooled by a closed fresh-water system thermostatically controlled at 180° F. The lub-oil capacity of each engine is 66 gal, and a suction pump provides pressure lubrication. The engines can be controlled singly or as a group by means of an electrically controlled hydraulic governor. Automatic devices indicate when the oil pressure is too low, or the cooling water temp too high, and an overspeed device is also fitted.

The associated electrical equipment is briefly described. Each engine drives a three-phase alternator which runs at 1000 r.p.m. and supplies 3000 V at 50 cycles/sec. The continuous and max outputs of each generator are 244 and 306 kW respectively. H. C. E.

778. 300 b.h.p. diesel mechanical locomotive. Anon. *Gas Oil Pwr*, 1950, **45**, 306.—This 40-ton four-wheel Hunslett locomotive has a starting effort of *ca* 23,000 lb, and can haul a load of 850 tons at 6 m.p.h. It is powered by a Crossley two-stroke EST-5 type engine with five cyl each of dimensions 7-inch bore and 9-inch stroke. The max output is 300 b.h.p. at 900 r.p.m. A reciprocating scavenging oil pump, and centrifugal water-pump, are fitted, and the engine is started by a 24-V electric motor.

Power from the engine is transmitted through a friction clutch and flexible coupling to a four-speed gear-box which provides for track speeds of $4\frac{1}{4}$, $6\frac{1}{2}$, $10\frac{1}{4}$, and 16 m.p.h. with corresponding max tractive efforts of 22,400, 14,700, 9300, and 5950 lb. Details of the locomotive construction are given. H. C. E.

779. Gas turbines in automobiles. W. A. Turunen. *S.A.E. Trans.*, Jan. 1950, **4** (1), 102–15.—Consideration of the application of the gas turbine to automobiles must be governed by the fact that existing power units are satisfactorily meeting current requirements and that, in order to compete with conventional units, the gas turbine must promise performance beyond that at present attained by reciprocating engines. A comparison of the calculated performance of a gas-turbine engine with that of a comparable reciprocating engine is presented. Handicaps to the installation of gas turbines are enumerated, together with advantages to be expected. Aspects treated include fuel consumption, recovery of exhaust heat, h.p., braking and torque characteristics, maintenance, exhaust and silencing problems, together with possible heavy-duty applications. J. G. H.

780. Gas turbine in a power station. Anon. *Mech. World*, 29.12.50, **128** (3337), 607.—In Feb. 1950 the initial six months' run of a power-station gas turbine was completed at the Huey station of the Oklahoma Gas and Electric Company. During that time the machine ran for 3912 hr, 15,486,000 kW hr were generated on an average load of 3959 kW and a max of 5000 kW. The average exhaust temp during the run was 776° F. The unit was tested during the initial run, and nothing developed during the run or was found during the subsequent inspection to prevent the unit from running indefinitely with little or no maintenance. The gas turbine is a nominally-rated, 3500-kW locomotive type of unit equipped with an air pre-cooler and a gas-heat exchanger for heating the steam-plant feed water. The fuel is natural gas and is supplied to the turbine at 150 p.s.i., the normal supply pressure, but a booster is installed in case of necessity. Lubrication is by simple pressure feed to all bearings from a main tank of 1200 gal capacity which contains the pump and oil coolers. A number of protective devices were added to the basic unit to make it completely automatic in starting and operation. The turbine is connected to the reduction gear

by means of a 15-inch long splined shaft to avoid any possibility of the turbine axial loading on the reduction-gear thrust-applying bearings. Sketches are given of the general arrangement of the boiler-feed system and service-water and well-water piping to the gas-turbine oil cooler, generator air cooler, and air precooler. A. S.

781. Machining gas turbine blading. Anon. *Mech. World*, 26.1.51, **129** (3341), 73.—Rapid production is possible if a turbine blade is so designed that its surfaces can be generated by a body of revolution, *e.g.*, grinding wheel or milling cutter, cutting over its full length. At the same time the adoption of such methods may impose severe limitations on blade design. This could be tolerated for turbine blades, but for compressor blades, it would lead to serious loss of performance. The only machining method which will provide blades unrestricted in profile is single-point tooling under the control of a master former, but this method is slow. Two devices are shown which allow complete freedom in design of profiles, and both these work on the cam-and-follower principle. One employs rotary and the other rectilinear motion of model and work, the former being suitable for light-alloy blades, and the latter for heavier work. These devices are completely illustrated and described, together with various modifications. A. S.

782. Choosing the right induction motor. E. H. Frederick. *World Oil*, Nov. 1949, **129** (8), 234–48.—The use of induction motors, up to 200 h.p. has become increasingly, extensive. Simplicity of construction has made them particularly adaptable to the petroleum industry. Mounting and frame dimensions have been standardized, as have the characteristics. Selection of the correct motor depends on these characteristics, and N.E.M.A. standards are tabulated. The different starting and running characteristics obtained by voltage and frequency variation, rotor bar inbedded depth and design variation, etc., are discussed. There are three main types of load. The first such as reciprocating compressors, requiring a definite amount of torque regardless of speed; the second, as in centrifugal blowers or pumps, in which torque demand varies as the square of the speed; the third, as in machine tools, where torque demand decreases as the speed increases. These need to be matched with the correct type of motor. A. H.

783. B.I.C.E.R.A. Seventh Annual Report. Anon. *Gas Oil Pwr*, 1950, **45**, 307–10.—The Report of the British Internal Combustion Engine Research Association covers the year ending March 1950, and describes the progress of research during this time. The field of study includes: fuel injection, fuel rating, combustion, instrument development, cyl-bore wear, tests of foreign engines, crankcase explosions, stress measurements and calculations, pressure chargers and pressure charging of engines, piston-type gas generators, rotary gas-turbine systems, engine-noise tests, use of low-grade fuels, lub oils, and starting at low temp. H. C. E.

784. Chromium as a wear preventive. G. H. Jackson. *Scientific Lubrication*, July 1950, **2** (7), 23–4.—The causes of wear in internal-combustion engines are outlined, and the ineffectiveness of fine-surface finish as a means of combating wear is remarked. Requirements for cyl-bore material are tabulated, and the marked suitability of chromium for this purpose is noted. The advantages of chromium-plated cyl liners are enumerated, and the corrosion- and abrasion-resistant properties of the metal are emphasized; the high coefficient of friction for chromium on chromium is also recorded. J. G. H.

785. Metal transfer from piston rings to cylinders during run-in. C. D. Strange and J. T. Burwell. *Scientific Lubrication*, Oct. 1950, **2** (10), 24–7.—Details are presented of an investigation of the micro-welding between rings and cyl walls during the "run-in" of a small water-cooled internal-combustion engine. Rings with radioactive wearing surfaces were used, and the results, obtained in the form of auto-radiographs, give a clear picture of the occurrences encountered during the "run-in" period. J. G. H.

Safety Precautions

786. Some aspects of air safety. C. H. Jackson. *J. Roy. Aero. Soc.*, 1950, **54**, 587.—Amongst other conclusions, those of main interest in the petroleum sphere are listed thus: (1) it may yet be shown that the introduction of kerosine fuels in turbine-engined aircraft will yield one of the biggest single improvements in safety; (2) turbine-engined aircraft will not introduce additional hazards, provided that proper operational procedures on fuel reserves are maintained; (3) the development of non-inflammable hydraulic fluids may give an increase in safety, for hydraulic fluid has been responsible for a number of near accidents. C. N. T.

787. Diesel engine crankcase safety precautions. C. C. Pounder. *Gas Oil Pwr*, 1950, **45**, 270–4.—The conditions under which crankcase explosions are likely to develop are discussed in detail. Safeguards are: (1) sufficient self-closing relief doors of correct weight and size, (2) a crankcase door which can be clamped in place, and (3) CO_2 drenching equipment. Other devices, such as the use of extraction fans, ventilation fans, flame traps, are discussed, but no opinion is given on their merits. H. C. E

788. Remote control for compressor station manifold. E. Sterrett. *World Oil*, Nov. 1949, **129** (8), 250–2.—Remote-controlled valves have been installed at a compressor station on the tower lines of Texas Eastern Transmission Corp. to facilitate valve closure in the event of fire. The plug-type valve on the suction side is closed hydraulically, the gate-type valve on the discharge is spun by an air motor, and various other vent-line valves, etc., are also operated by air motor. Enough gas is bled from the lines to maintain the operating pressure at 275 lb gauge at all times. A. H.

789. The hazards of synthetic plastics. J. V. Grimaldi. *Mech. Engng*, Dec. 1950, **72**, 987.—The growing prominence of plastics in the industrial realm has recently fixed attention on the fire hazards associated with the manufacture, use, and storage of plastic materials. The nitrocellulose in pyroxylin (one of the first plastics) burns violently, but most modern plastics do not have rapid-burning characteristics, in fact many have the quality of being relatively difficult to ignite except when suspended in air as a fine dust. However, because of the general term "plastics" many people think of the fire hazard without regard to the type of plastic involved. At the same time it is important to encourage such respect for fire hazards, as this might eliminate certain accidents due to thoughtlessness. Explosion and fire hazards are greatest in the manufacture of resins and preparing the melting compounds for fabrication purposes. Dust and faulty operation at high temp and pressures offer the greatest hazards in plastics fabrication. Hazards are also found in the recovering and control of solvents employed in spraying, dipping, coating, and laminating operations. The recovery of solvents often concentrates the impurities present, tending to produce lower boiling temp and reduced fl. pt. and ignition temps than existed for the initial solvent. Generally speaking the greatest hazards exist in the fabrication of plastic products and the grinding of scrap plastic. The burning of most of the plastics themselves should not cause any more concern than the burning of wood or woollen fabrics, or fats and oils. The toxic products of combustion are for the most part of greater danger than carbon monoxide, and this compound must be considered in the case of any fire. A. S.

Miscellaneous

790. Fourth World Power Conference, London, 1950. Anon. *Gas Oil Pwr*, 1950, **45**.—Extended abstracts are given of the following papers read at the above conference: "Methods of power production involving the use of auxiliary gas turbines," by M. Roy, p. 269; "Modern trends in oil engine designs," by I. Wans, p. 277; "Land type gas turbines," by D. M. Smith, p. 274; "On the choice of fuel for internal combustion engines," F. Picard, p. 283; "Summary of current developments in large diesel and gas engines," by R. L. Boyer, p. 275; "Summary of current developments in small

diesel engines," by M. R. Bennett, p. 276; "Recent developments in light-weight spark-ignition and compression ignition piston engines," by W. A. Robotham, p. 279. H. C. E.

791. Is petroleum a Soviet weakness? D. B. Shimkin. *Oil Gas J.*, 21.12.50, **49** (33), 214.—A review is given of the oil production, reserves, weakness, and strength of the U.S.S.R., based on published and unpublished information available to the Russian Research Centre, Harvard University.

Tables list oil and gas fields, average composition of gases, specifications of selected Soviet crude oils, comparative specifications of Russian and U.S.A. gasolines, U.S. exports to Russia, and location and capacity of U.S.S.R. pipelines. G. A. C.

792. Iraq oil industry moves toward broad expansion. E. L. Lomax. *World Petrol.*, 1950, **21** (10), 53–5.—Pipeline construction and crude-oil production in the Kirkuk field are discussed. Transportation of crude via pipeline, existent or under construction, is 25 million tons/year (including 6 million tons which could be pumped to Haifa). E. B.

793. Italy has big refinery expansion under way. Anon. *World Petrol.*, 1950, **21** (8), 88.—A summary of expansion programme. Completion of projects will increase plant capacity to 1,200,000 b.d. E. B.

794. Mexico's distribution problem eased by new Salamanca refinery. R. O. Mena. *World Petrol.*, 1950, **21** (10), 48–52.—Description of the 30,000-b.d. refinery located at Salamanca to serve central Mexico with gas, motor fuel, kerosine, gas oil, and fuel oil. Place in Pemex development plan is discussed. E. B.

795. World production resumes upward trend. D. M. Duff. *Oil Gas J.*, 21.12.50, **49** (33), 204.—A review of world oil production shows an increase of over 11% over 1949 figures, bringing daily average for year to 10,370,000 brl.

Charts show production in millions of b.d. for producing areas. G. A. C.

796. World supply–demand situation now viewed with more optimism. A. D. Stewart. *Oil Gas J.*, 21.12.50, **49** (33), 192.—A review is presented of the world oil situation, taking into account the change in world outlook, foreign-currency situation, world demand, expansion plans, petroleum movements, and maintenance of balance of crude producibility and refining facilities.

Twenty tables illustrate the article. G. A. C.

797. World-wide oil report. D. M. Duff. *Oil Gas J.*, 21.12.50, **49** (33), 154.—Current activities and operations for all divisions of the oil industry are presented country by country, excluding the Soviets. The Middle East, the Far East, Western Europe, Canada, Mexico, and South America are reported on, figures for production and refining capacity being included. G. A. C.

798. $7·5 billion refinery expansion forecast for the next ten years. W. F. Bland. *Petrol. Process.*, 1950, **5** (9), 933–8.—As the result of a survey carried out by *Petrol. Process*, the estimated expansion of the U.S. petroleum industry over the next decade is given as an additional 2·5 billion b.d. crude refining capacity, at an annual total cost of $\$\frac{3}{4}$ (U.S.) billion. By 1960 it is forecast that thermal cracking will be almost completely replaced by cat cracking, with greater attention being paid to catalytic reforming and feed preparation for cracking feed stock. Gasoline O.N. rating is expected to rise to 90 to 91 Research for regular and 97 to 98 for premium grades. Various other estimates are compared. D. W. F.

799. Survey of oil refineries. Anon. *Oil Gas J.*, 21.12.50, **49** (33), 322.—A summary of world refining capacity is presented by countries, showing number of operating refineries, crude-oil-capacity and cracking-capacity ratings in b.d., and refineries under construction. G. A. C.

800. Oil refineries of the world. Anon. *World Petrol.*, 1950, **21** (8), 92, 94, 100–1.—Tabulation showing present capacities and type of oil refineries outside the U.S.A. E. B.

801. Petroleum distribution and marketing in the United Kingdom. C. M. Merrick. *I.P. Review*, 1950, **47**, 366.—In 1900, 80% of petroleum products imported to the U.K. was used for paraffin lamps, the balance being mainly lubricants. By 1914, motor spirit and fuel oils had become increasingly important. Distribution of motor spirits was mainly by 2-gal-cans, but the kerb-side petrol-pump appeared in 1920. After the 1914–18 war, the main development was the introduction of bulk distribution of all petroleum products. There was a series of strategically-placed seaboard installations feeding a network of depots all over the country from which retailers and users were supplied by tank wagon. From 1939 to 1948, the Petroleum Board took over the distribution of " Pool " grades of all products. Details of the present-day distribution methods for motor spirit, aviation fuel, kerosine, fuel oil, gas oil, bunker fuel, and bitumen, are given. Various aspects of control, branding, contracts, and pricing are discussed. R. H.

802. The inventor and the employer. R. F. McKay. *Mech. World*, 15.12.50, **128** (3335), 563.—It is impossible to follow in practice the fundamental principle that an inventor can do as he pleases with his own inventions. State security and defence regulations may have a strong bearing on the publication of inventions affecting the safety of the realm. In other words, a secrecy ban might be imposed on the invention. Furthermore, it has been established that an employer is the beneficial owner of some at least of the inventions of his employees. It does not follow, however, that the inventions of all employees belong to the employer. In this respect inventions by research workers or draughtsmen in the course of their employment are the property of their employer, even though there is no written contract to this effect. Only if the invention is entirely outside the range of the employer's business are the rights of the invention the property of the employee. Between these two extremes of the employer having all or none of the rights in the inventions of this group of employees come intermediate cases which can only be judged on individual merits. A government department may give its employees rights in an invention so long as the use for the Crown is reserved. As regards technical staff engaged in managerial or executive work, any inventions made by them are the property of employees exclusively unless there is a contract which allows the employer to have the whole or some part of the rights of the invention. As regards operatives, their inventions belong exclusively to them unless there is a written contract to the contrary. This is true even though the invention is made in the employers time and with the employers tools and materials. Inventions made by salesmen are their property unless a contract states otherwise. A. S.

803. Choice of chemical balance. G. F. Hodsman. *Chem. Prod.*, Dec. 1950, **13** (13 475.—In choosing a chemical balance for a particular purpose, it is not always mos satisfactory, technically or economically, to decide upon the balance giving the highes precision. For instance, in general, the higher the precision of a balance the slowe is the weighing operation and the smaller its capacity.

Based on such considerations as this and on actual construction of different types of balance, the author indicates the factors which should be taken into account when purchasing a chemical balance. O. M.

BOOKS RECEIVED

Directory of International Scientific Organizations. Paris: United Nations Educational, Scientific, and Cultural Organization, 1950. Pp. xiii + 223.

A year-book giving information on some 300 international organizations whose activities deal with the various branches of science. In the applied science section twenty pages are devoted to organizations in the engineering field.

The Royal Dutch Petroleum Company, 1890 to 1950. The Hague: The Company, 1950. Pp. 205.

The English language edition of the book published by the Royal Dutch Petroleum Company on the occasion of its Diamond Jubilee.

The Institution of Mechanical Engineers, Proceedings. War Emergency issues, Nos. 47–54, 1949. London: The Institution. Pp. vii + 262.

Contents include: "The Surface Roughness of Bearing Surfaces and its Relation to Oil Film Thickness at Breakdown," by A. Cameron; "Producer Gas for Road Transport," by T. F. Hurley; "The Ideal Performance of Petrol Engines," by A. S. Leah; "Some Properties of the Compression Shock as in Turbine and Compressor Blade Passages," by I. M. Davidson; "The Total-heat, Air-ratio Diagram: A new Method for the Calculation of Gas-Turbine Cycles," by Ernst Schmidt; and "Some Developments in Instrumentation for Air-flow Analysis," by K. W. Todd.

British Chemicals and Their Manufacturers. London: The Association of British Chemical Manufacturers, 1951. Pp. 169.

A new and revised edition of this useful directory which is issued every two years. A directory of members, in which each manufacturer is designated by a code number, is followed by a classified list of products which includes the code number of the manufacturers of each product. There are also lists of trade names and trade marks.

Copies of the directory are available, free of charge, to persons or firms genuinely interested in the purchase of chemicals, and enquiries should be addressed to the Association at 166, Piccadilly, London, W.1.

Elements of Reservoir Engineering. S. J. Pirson. New York: McGraw-Hill Book Co. Inc., 1950. Pp. vii + 411.

Process Heat Transfer. D. Q. Kerr. New York: McGraw-Hill Book Co. Inc., 1950. Pp. xii + 871.

Instrumental Methods of Analysis. H. H. Willard, L. L. Merritt, and J. A. Dean. New York: D. Van Nostrand Co. Inc. Pp. 247.

I.C.I. Engineering Codes and Regulations, Group C (Electrical) Volume 1·4-Portable and Transportable Plant and Equipment. London: Imperial Chemical Industries Ltd., 1950. Pp. 27.

API Standards Supplements and Bulletins. (American Petroleum Institute, Dallas, Texas).

API Std 11B. (10th ed., Oct. 1950). **Sucker Rods.** Pp. 27. $1.00.

RP 11BR. (1st ed., Sept. 1950). **Care and Use of Sucker Rods.** Pp. 1. 10 cents.

API Std 12C. (9th ed., Oct. 1950). **Welded Oil Storage Tanks.** Pp. 65. $1.25.

Bul S2. (28th ed., Dec. 1950). **Official List, Publications of API Division of Production.** Pp. 11.

APPLICATIONS FOR MEMBERSHIP OR TRANSFER

MARCH 1951

The following have applied for admission or transfer to the Institute. In accordance with the By-laws, the proposals will not be considered until the lapse of at least one month after the publication of this *Journal*, during which time any Fellow, Member, Associate Fellow, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of the candidate.

The object of this information is to assist the Council in grading the candidate according to the class of membership.

The names of candidates' proposers and seconders are given in parentheses.

Applications for Membership

BOYD, James Wennington, deputy fields chemist, Iraq Petroleum Co. Ltd. (*H. A. Freeman ; A. H. R. Grimsey.*)

COOPER, John March, assistant managing director, Kuwait Oil Co. Ltd. (*C. A. P. Southwell ; E. C. Masterson.*)

CURTIS, David Sacheverrell, superintendent, Stores Dept, Kuwait Oil Co. Ltd. (*E. Boaden ; R. M. S. Owen.*)

DICKINS, Geoffrey Arthur, head of Analytical Dept, Vacuum Oil Co. Ltd. (*E. A. Evans ; H. M. Davies.*)

ECKER, Howard, consultant. (*R. W. Curtis ; G. Sell.*)

HENNING, Jack, chemist, Anglo-American Oil Co. Ltd. (*E. J. Boorman ; J. W. Clarke.*)

JEENS, Kenneth Pilkington Hinton, chief buyer, Messrs. E. B. Badger & Sons (G.B.) Ltd. (*J. T. T. Robinson ; T. W. Muncaster.*)

LENNIE, Keith Stuart, engineer, Bahrein Petroleum Co. Ltd. (*R. H. Meeker ; R. L. Vernier.*)

LONG, Kenneth James, assistant port captain, Esso Transportation Co. Ltd. (*R. S. Coulson ; T. G. Kidd.*)

MARTIN, Gerald, student technician, Camborne School of Mines. (*G. A. Whitworth ; G. Sell.*)

NEWBERY, Gerald Bernard, technical buyer, Messrs. E. B. Badger & Sons (G.B.) Ltd. (*J. T. T. Robinson ; T. W. Muncaster.*)

NEWLYN, Henry Dixon, manager, Supplies & Shipping Dept, Fina Petroleum Products Ltd. (*W. F. Jelffs ; A. F. Wilson.*)

PARK, George McKechnie, technical officer, Ministry of Fuel & Power. (*E. J. Sturgess ; D. R. Howfin.*)

PRICE, Albert Edmund, assistant to chief engineer, Iraq Petroleum Co. Ltd. (*E. A. Satchell ; D. B. Bremner.*)

TAYLOR, Alexander Harte, technical assistant and buyer, Anglo-Iranian Oil Co. Ltd. (*W. Wade ; T. J. F. Armstrong.*)

THORPE, Robert Claude (Lt.), M.T. Officer, Royal Marines.

WANKLYN, Patrick Rawson, installation manager, Shell Co. of Syria Ltd. (*R. Batie ; A. McL. Knox.*)

WARD, John Mason, head of Chemistry Section, British Electricity Authority. (*P. M. Gossling ; C. H. Thompson.*)

Transfers

CLARKE, Arthur Henry, chemist, Geochemical Laboratories Ltd. (*H. B. Milner ; D. C. Broom.*) (*Associate Member to Fellow.*)

CULLINGHAM, Ernest Keith, geologist, Anglo-Iranian Oil Co. Ltd. (*G. M. Lees; G. Sell.*)

EDGHILL, Charles Murray, production engineer, Anglo-Ecuadorian Oilfields Ltd. (*R. Ogilvie; P. H. H. de Pass.*) (*Student to Associate Fellow.*)

HANCHARD, Kenneth William, marketing assistant, Vacuum Oil Co. Ltd. (*S. J. M. Auld; R. W. L. Fox.*) (*Student to Associate Member.*)

WETHERILL, Kenneth, production engineer, Shell C.P.C. Venezuela. (*J. E. Smith; L. C. Stevens.*) (*Student to Associate Fellow.*)

WILLMOTT, Ivor Alan, project engineer, "Shell" Refining & Marketing Co. Ltd. (*R. W. J. Smith; J. L. Black.*) (*Student to Associate Fellow.*)

NEW MEMBERS

The following elections have been made by the Council in accordance with the By-laws.

Elections are subject to confirmation in accordance with the By-laws.

As Member

KING, A. L.

As Associate Fellows

CURTIS, G. D.
FAWCETT, P.
GEYRA, I.
GREAVES, W. C.
LAHIRI, B. N.
PILLING, R. W.

Transferred from Associate Member to Associate Fellow

ROE, J. G. A.

Transferred from Students to Associate Fellows

CHARLES, E. J.
FAULKNER, B.A.

As Associate Members

BAYLEY, L. C. J.
COBBETT, R. F.
HILL, R. W.
TANNER, G. H.
UDEN, R.

As Student Member

MILLER, L. H.

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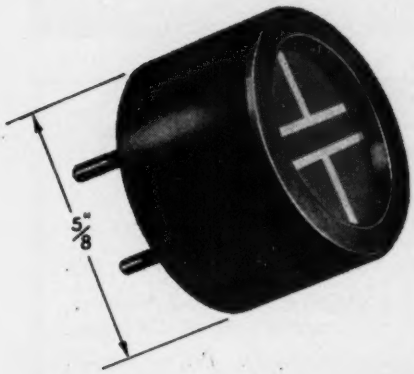

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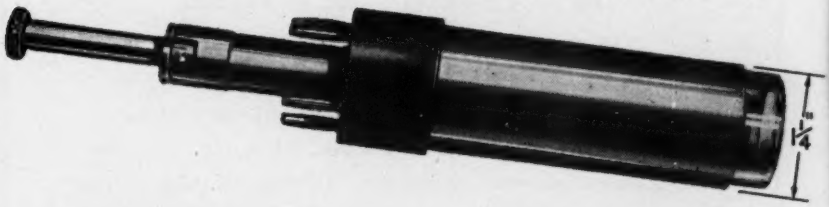

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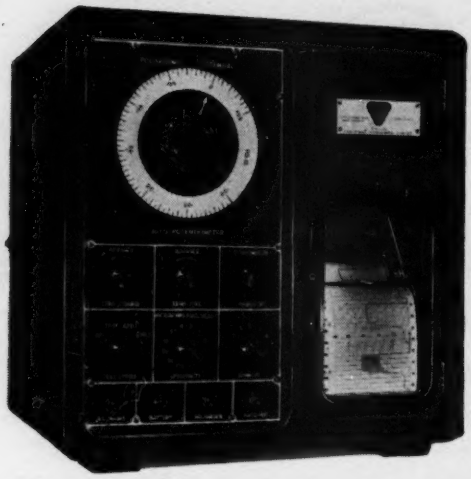

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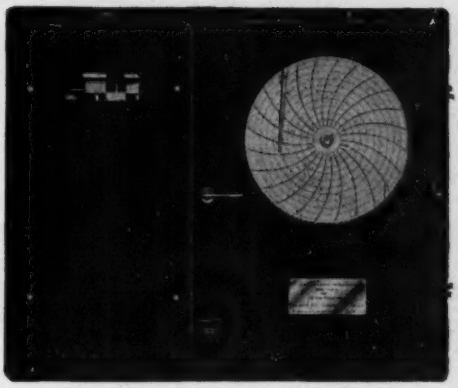

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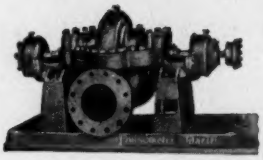

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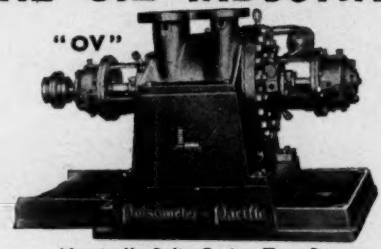

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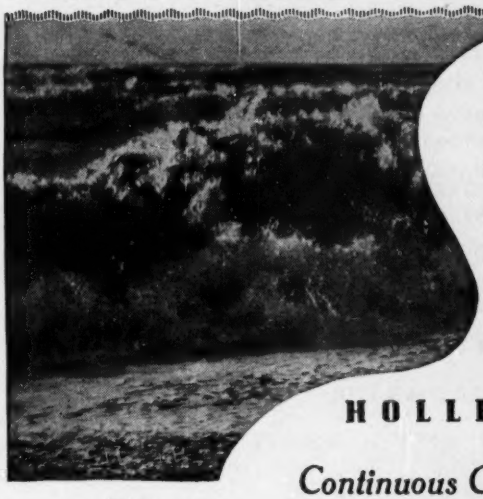

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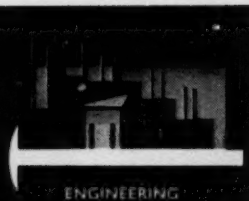

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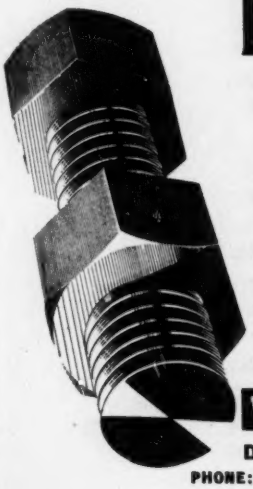

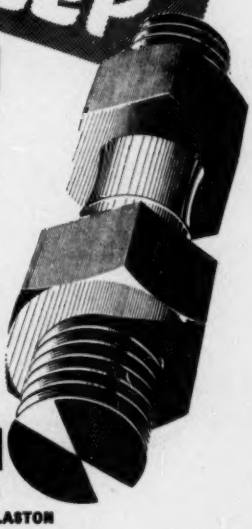

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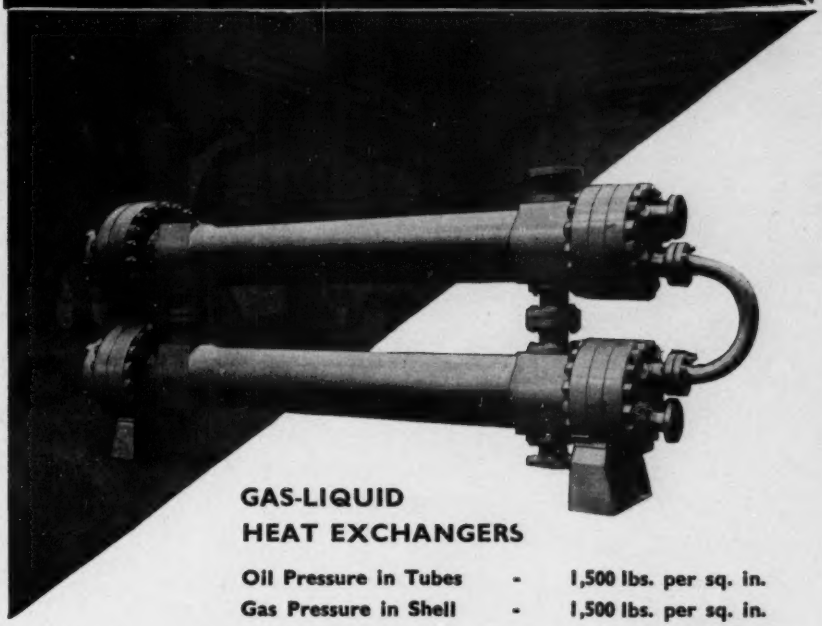

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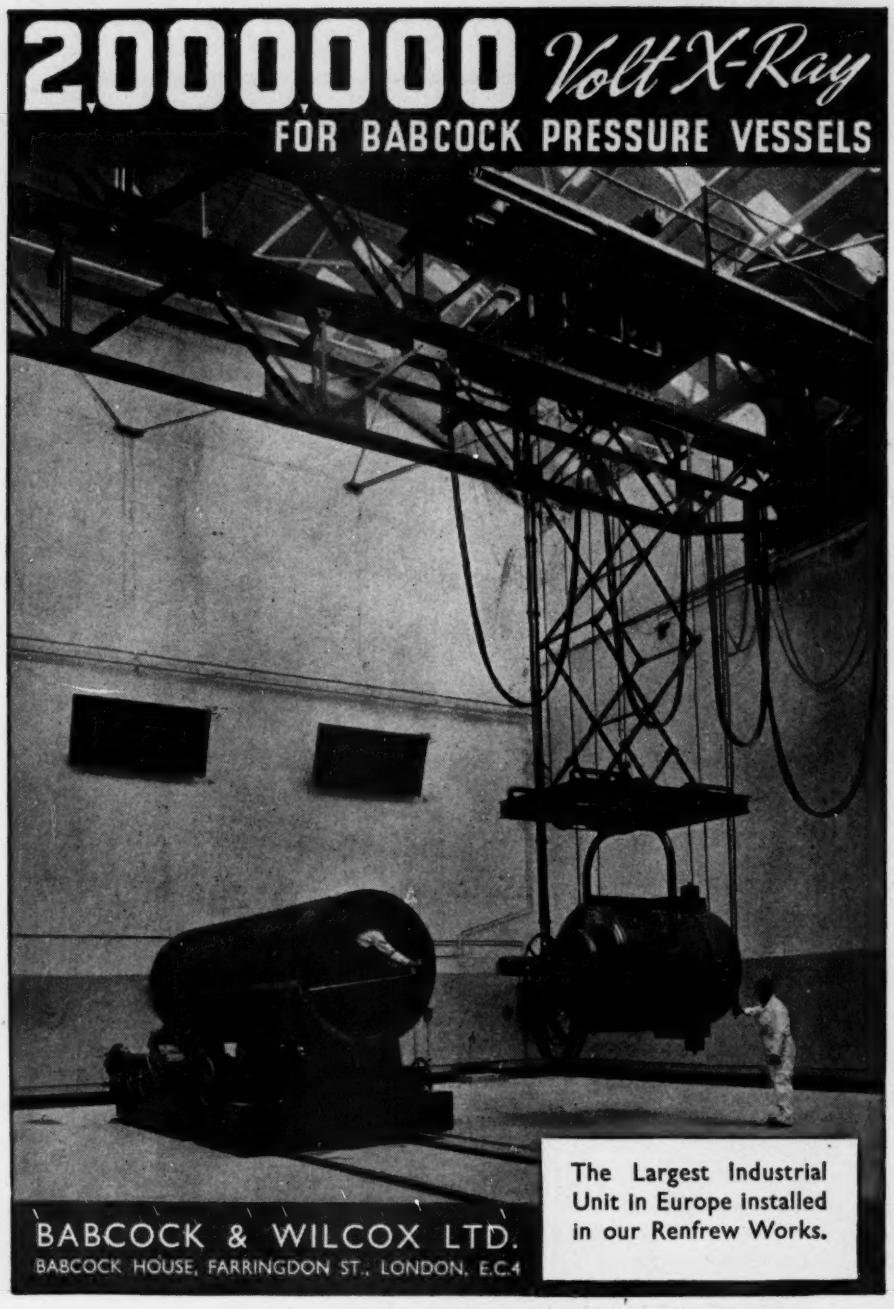
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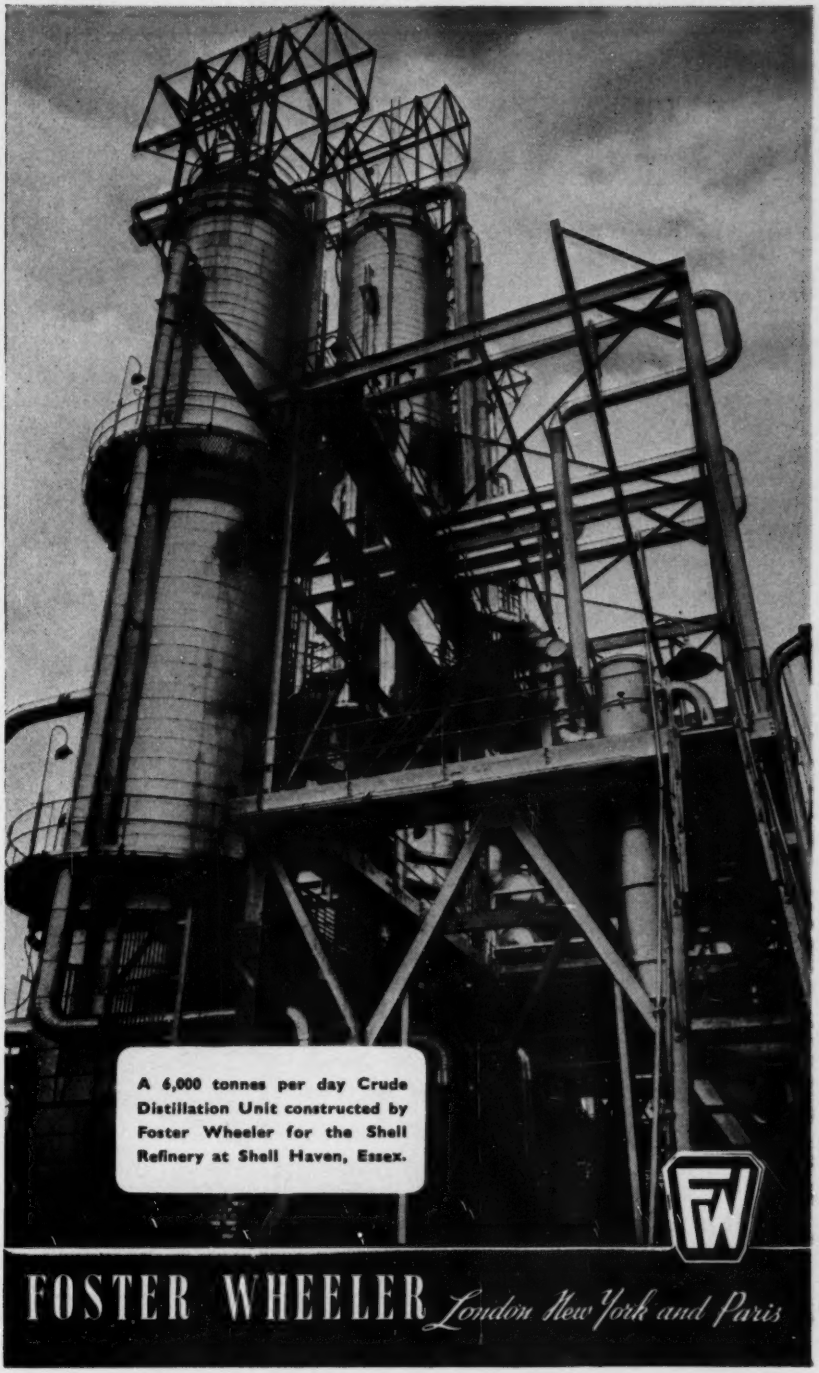
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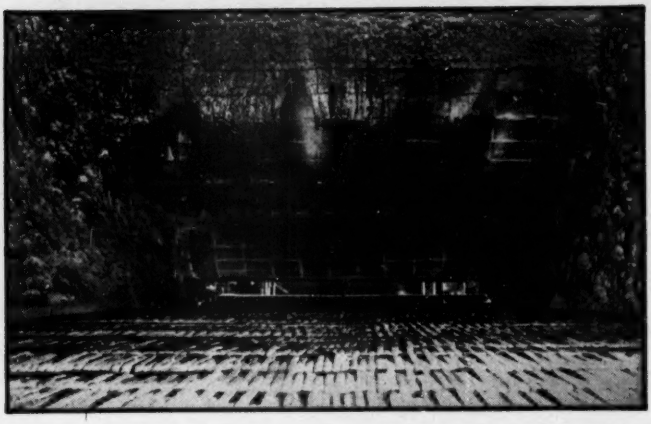

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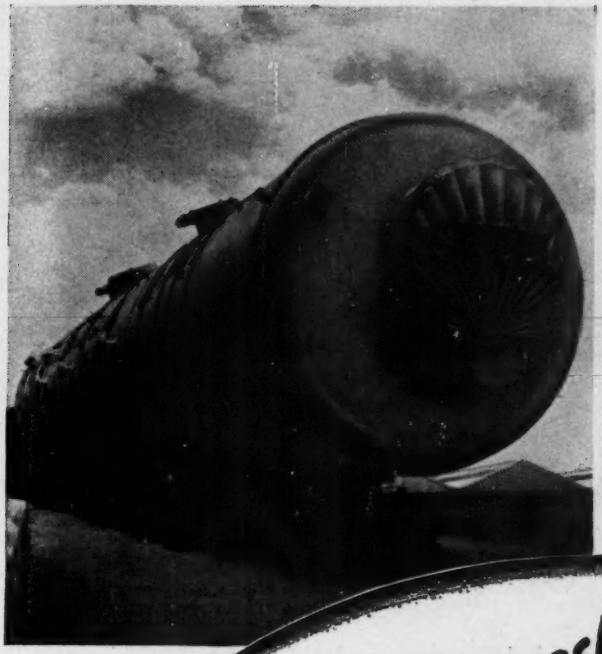

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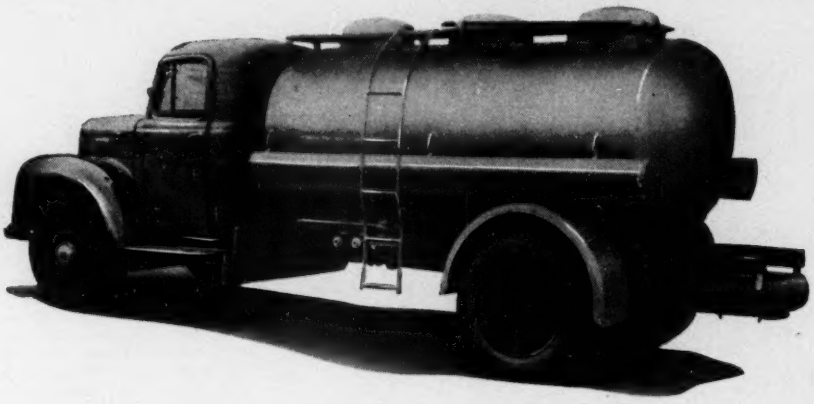

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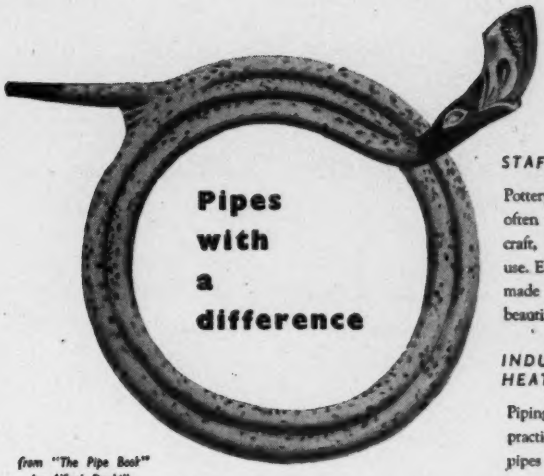

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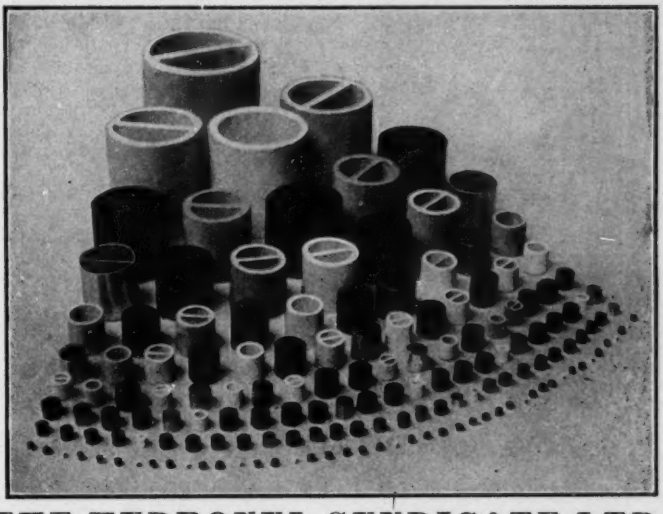

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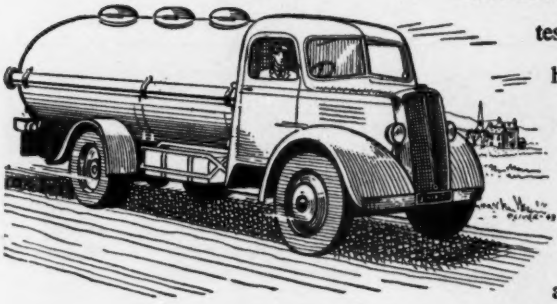

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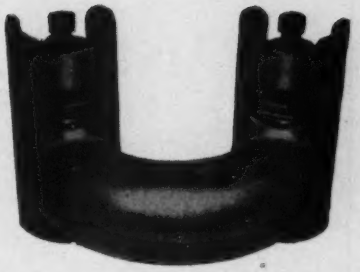

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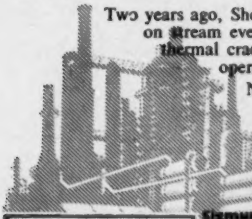

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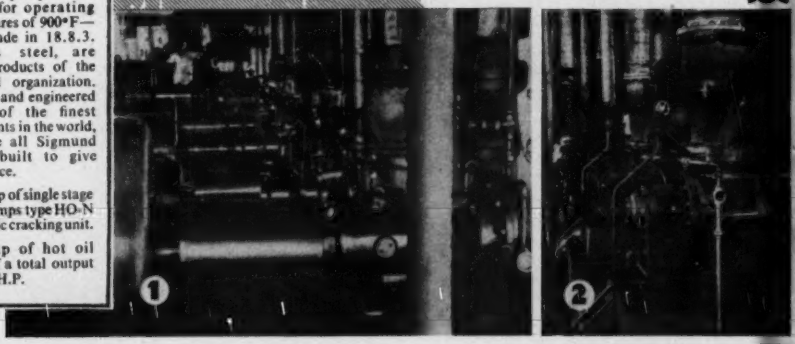

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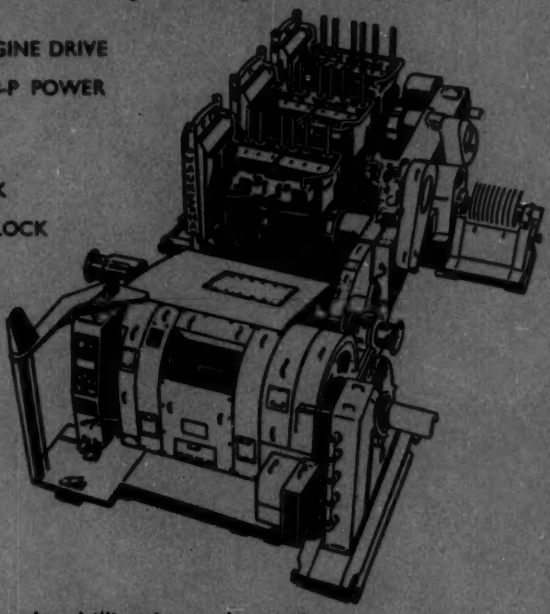

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